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Supporting Information

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Total Syntheses of (−)-Transtaganolide A, (+)-Transtaganolide B, (+)-Transtaganolide C, and (−)-Transtaganolide D and Biosynthetic Implications**

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Table of Contents

I. Materials and Methods **S3**

II. Experimental Procedures **S3**

III. Comparison of Spectral Data for Synthetic and Reported Transaganolide A (**1**) and B (**2**) **S17**

IV. Crystal Structure Analysis of methyl ester **33** **S20**

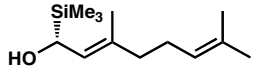
V. CD Data of Methyl Ester **33** **S30**

VI. Spectra **S31**

I. Materials and Methods

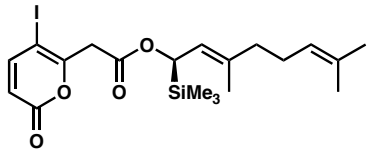
Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Chemicals were purchased from Sigma-Aldrich Chemical Company and used as received. $Pd(PPh_3)_4$ was prepared using known methods. Thin layer chromatography (TLC), both preparatory and analytical, was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, I_2, or $KMnO_4$ staining. Analytical super critical fluid (SFC) chromatography was performed using a Thar SFC and either Chiralpak IA or AD-H columns. Preparatory SFC was performed with a Jasco SFC and a prep AD-H columd (21 x 250 mm, 5mic part# 19445). ICN Silica gel (particle size 0.032-0.063 mm) was used for flash chromatography. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz) or on a Varian Unity Inova 500 (at 500 MHz). ^{1}H NMR spectra are reported relative to $CDCl_3$ (7.26 ppm). Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), integration. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept. = septet, m = multiplet, bs = broad singlet. ^{13}C NMR spectra are reported relative to $CDCl_3$ (77.0 ppm). FTIR spectra were recorded on a Perkin Elmer SpectrumBX spectrometer and are reported in frequency of absorption (cm^{-1}). HRMS were acquired using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), or multimode-ESI/APCI. Crystallographic data were obtained from the Caltech X-Ray Diffraction Facility.

II. Experimental Procedures



Enantioenriched allyl silane 16. To a 23 °C solution of known diisopropyl geraniol carbamate[1] (**15**, 519 mg, 1.84 mmol) in toluene (9.2 mL, 0.2M) was added freshly distilled (–)-sparteine (635 μL, 2.76 mmol) and TMSCl (352 μL, 2.76 mmol). The solution was then cooled to –78 °C and a solution of 2.5M *n*-BuLi in hexanes (1.1 mL, 2.76 mmol) was added dropwise. The reaction was allowed to stir at –78 °C for 3 hours. The reaction was then quenched at –78 °C by slow addition of MeOH (250 μL) and allowed to warm to 23 °C. The reaction was washed with saturated NH_4Cl (2 x 10 mL). Aqueous layers were combined and back extracted with Et_2O (3 x 20 mL). The combined organics were than washed with brine (20 mL), dried over $MgSO_4$, and concentrated by rotary evaporation. This crude oil could be taken on without further purification. Purification, if desired, was done via column chromatography (ethyl acetate in hexanes 2%⇒10% on SiO_2) to yield 602 mg (92% yield) of allyl silane **10**, as a colorless oil.

Allyl silane **10** (2.36 g, 6.7 mmol) was dissolved in THF (67 mL, 0.1M with respect to substrate) and hexanes (40 mL, 1.0 M with respect to DIBAL-H) and cooled to 0 °C. To this 0 °C solution was slowly added neat DIBAL-H (7.1 mL, 40.2 mmol) dropwise. After the addition, the reaction was warmed to 23 °C and stirred for 6 hours. The reaction was then cooled to 0 °C and slowly quenched with saturated aqueous Rochelle's salt (35 mL) with vigorous stirring. After addition of Rochelle's salt, the reaction was allowed to warm to 23 °C and celite (10 g) was added. The suspension was vigorously stirred for another 5 minutes and then filtered through a small pad of celite. The organic layer was collected, washed with saturated brine (35 mL), dried over $MgSO_4$, and concentrated by rotary evaporation. The crude oil could be taken on without further purification. If desired, purification was accomplished by column chromatography (ethyl acetate in hexanes 2%⇒20% on SiO_2) to yield 1.38 g (91% yield) of colorless oil **16**. $[\alpha]_D^{20}$ = +69.71 (*c* 1.00 in $CHCl_3$). Enantiomeric excess (*ee*) was determined for **13** inferred for **16**. All other spectral data matches the literature.[1]



Pyrone ester 13. To a solution of enantioenriched geraniol derivative **16** (202 mg, 0.89 mmol) in MeCN (9 mL, 0.1 M) at 0 °C was added sequentially pyrone acid **17** (300 mg, 1.07 mmol) and DCC (221 mg, 1.07 mmol). After 20 min at 0 °C, the reaction was filtered through a plug of celite washing with MeCN. The filtrate was collected and concentrated by rotary evaporation and the crude oil was purified by column chromatography (ethyl acetate in hexanes 2%⇒10% on SiO_2) to yield 384 mg (88% yield) of ICR/DA precursor **13** as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 9.7 Hz, 1H), 6.06 (d, *J* = 9.7 Hz, 1H), 5.42 (d, *J* = 10.4 Hz, 1H), 5.14 (dq, *J* = 10.4, 1.2 Hz, 1H), 5.04 (tm, *J* = 6.2, 1H), 3.76 (s, 2H), 2.16 – 2.00 (m, 4H), 1.66 (d, *J* = 1.4 Hz, 6H), 1.59 (d, *J* = 1.2 Hz, 3H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 160.6, 158.6, 151.4, 138.0, 131.8, 124.1, 120.9, 116.1, 70.5, 69.7, 43.1, 40.0, 26.6, 25.9, 17.9, 17.0, –3.7.

FTIR (Neat Film NaCl) 2959, 2923, 2854, 1741, 1607, 1546, 1445, 1404, 1382, 1336, 1293, 1273, 1249, 1206, 1170, 1134, 1062, 1016, 960, 908, 842, 819, 750 cm^{-1}; HRMS (Multimode-ESI/APCI) m/z calc'd for $C_{20}H_{28}IO_4Si$ $[M–H]^-$: 487.0807, found 487.0821. 90% ee; SFC conditions: 3.0% IPA, 2.5mL/min, AD-H column, t_R (min): major = 7.02, minor = 7.79.

A portion of this material was then separated by preparatory chiral SFC to obtain >99% ee material; $[\alpha]_D^{20}$ = +69.71 (*c* 1.00, $CHCl_3$, >99% ee).

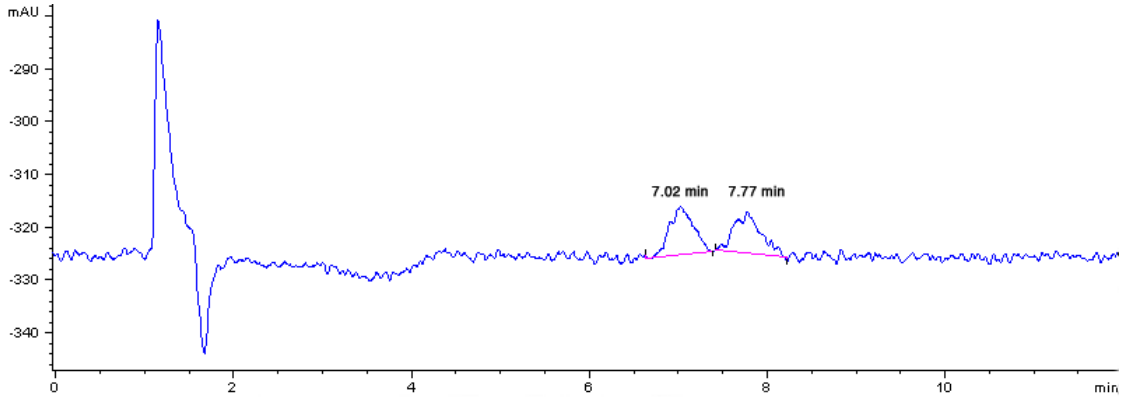


Figure SI-1. Racemic SFC trace of compound **13**.

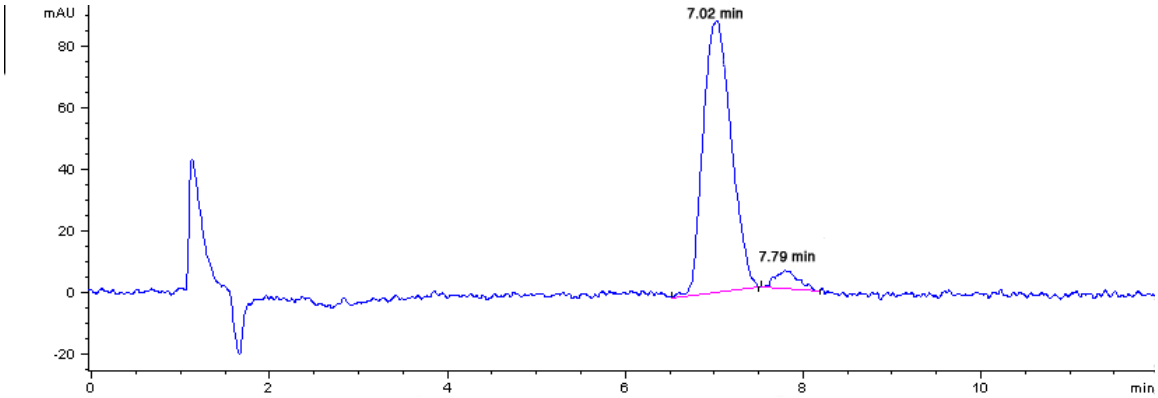
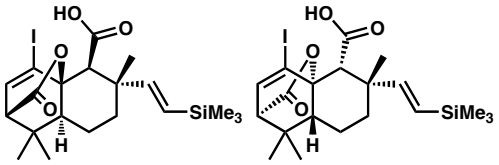


Figure SI-2. Enantioenriched SFC trace of compound **13**.



Vinyl silanes 18 and 19. To a 23 °C solution of pyrone ester **13** (384 mg, 0.79 mmol) in toluene (4 mL, 0.2M) in a 500 mL sealed tube was added *N,O*-bis(trimethylsilyl)acetamide (BSA) (384 μL, 1.58 mmol) and NEt_3 (11 μL, 0.08 mmol). The reaction mixture was heated to 110 °C and stirred for 20 minutes. The solution was then cooled to 23 °C and diluted with toluene (450 mL), leaving ample headspace in the sealed tube to allow for solvent expansion. The reaction mixture was then re-heated to 100 °C and stirred for 4 days until complete as determined by NMR analysis. The reaction mixture was then cooled to 23 °C and 0.02% $HCl_{(aq)}$ (20 mL) was added and the reaction mixture was stirred vigorously for one minute. The organic phase was then separated and washed with 0.02% $HCl_{(aq)}$ (3 x 25 mL) making sure aqueous phase remains acidic. The aqueous phases were then combined and back extracted with ethyl acetate (3 x 30 mL) and all organic phases were combined, dried with Na_2SO_4, and concentrated by rotary evaporation. The crude oil was purified by column chromatography (diethyl ether in hexanes with 0.1% AcOH 10%⇒20% on SiO_2) to yield

294 mg (77% yield) of a 3:1 diastereomeric mixture of ICR/DA products **18** and **19** as white solids.

Major (18): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (d, J = 6.9 Hz, 1H), 6.12 (d, J = 18.9 Hz, 1H), 5.64 (d, J = 18.9 Hz, 1H), 3.01 (s, 1H), 2.97 (d, J = 6.9 Hz, 1H), 1.72–1.21 (m, 5H), 1.28 (s, 3H), 1.08 (s, 3H), 1.00 (s, 3H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 170.8, 155.4, 140.2, 125.3, 98.0, 84.7, 59.3, 56.7, 48.1, 41.3, 38.2, 36.9, 29.9, 24.6, 20.8, 18.5, –1.0.

Minor (19): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (d, J = 6.8 Hz, 1H), 6.44 (d, J = 19.2 Hz, 1H), 5.68 (d, J = 19.2 Hz, 1H), 2.95 (d, J = 6.8 Hz, 1H), 2.95 (s, 1H) 1.96 (dt, J = 13.5, 3.1 Hz, 2H), 1.72–1.21 (m, 3H), 1.31 (s, 3H), 1.04 (s, 3H), 0.99 (s, 3H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 169.9, 148.0, 140.5, 127.8, 97.5, 84.8, 61.2, 56.8, 47.9, 40.5, 38.1, 37.0, 29.7, 24.6, 20.7, 18.5, –1.1.

FTIR (Neat Film NaCl) 3075, 3014, 2955, 2671, 2545, 1755, 1713, 1612, 1464, 1455, 1415, 1397, 1386, 1373, 1338, 1286, 1246, 1218, 1174, 1133, 1103, 1048, 1016, 990, 967, 932, 903, 867, 838, 796, 757 cm^{-1}; HRMS (Multimode-ESI/APCI) m/z calc'd for $C_{20}H_{30}IO_4Si$ $[M+H]^+$: 489.0953, found 489.0952; $[\alpha]_D^{20}$ = +13.28 (*c* 2.00, $CHCl_3$, 90% ee of **18**, 80% ee of **19**); SFC conditions: 15.0% IPA, 2.5 mL/min, IA column, t_R(min): **18)** major = 4.85, minor = 5.64; **19)** minor = 4.05, major = 6.05.

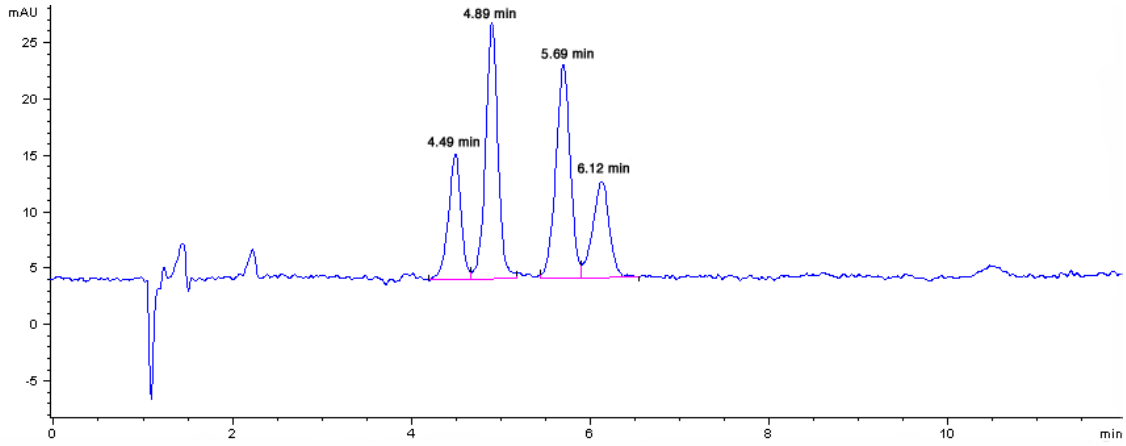


Figure SI-3. Racemic SFC trace of compounds **18** and **19**.

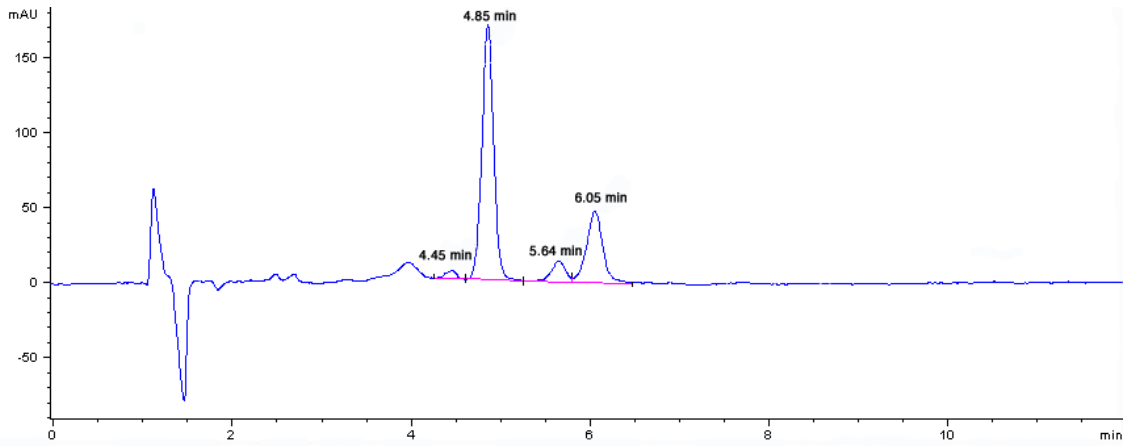
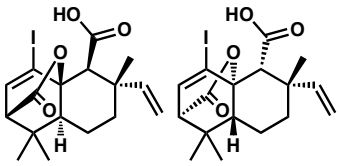
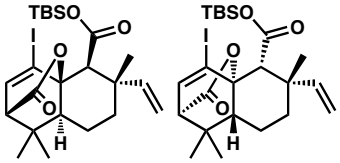


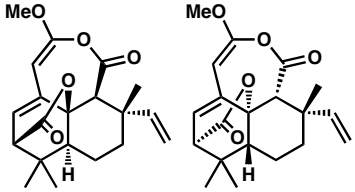
Figure SI-4. Enantioenriched SFC trace of compounds **18** and **19**.



Iodoacids 12a and 12b. To a 23 °C solution of vinyl silanes **18** and **19** (36.5 mg, 0.075 mmol) in MeCN (1.5 mL, 0.05M) was added $HBF_{4(aq)}$ (48% w/w, 75 μL, 0.60 mmol). The reaction was stirred for 4.5 hours and then diluted with ethyl acetate (15 mL). The organic layer was then washed with 0.02% $HCl_{(aq)}$ (3 x 5 mL). The aqueous phases were combined and back extracted with ethyl acetate (3 x 5 mL). The combined organic phases were dried over Na_2SO_4 and concentrated by rotary evaporation. Purification by column chromatography (ethyl acetate in hexanes with 0.1% AcOH 5%⇒30% on SiO_2) yielded 27.5 mg (89% yield) of a 4:1 diastereomeric mixture of the desilylated tricycles **12a** and **12b** as white solids. $[\alpha]_D^{20}$ = +42.73 (*c* 1.00 in $CHCl_3$). All other spectral data matches the literature. [2]



TBS-esters 12c and 12d. To a 23 °C solution of iodoacids **12a** and **12b** (46 mg, 0.11 mmol,) in DMF (300 μL, 0.35M) were added sequentially imidazole (76 mg, 1.1 mmol) and TBSCl (84 mg, 0.55 mmol). The reaction was warmed to 40 °C and then stirred for 12 hours. The solution was then diluted with brine (1 mL) and extracted with Et_2O/hexane (1:1) (3 x 2 mL). The combined organic extracts were washed with saturated aqueous $KHSO_4$ (1 mL) and then with brine (3 x 1 mL). The combined organics were dried over Na_2SO_4, and concentrated by rotary evaporation. The crude oil was purified by column chromatography (ethyl acetate in hexane 10%⇒50% on SiO_2) to yield 39 mg (66% yield) of a 4:1 mixture of diastereomers **12c** and **12d** as white powders. $[\alpha]_D^{20}$ = +41.42 (*c* 1.00 in $CHCl_3$). All other spectral data matches the literature. [2]



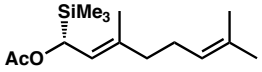
Transtaganolides C and D (3 and 4). In a nitrogen filled glovebox, to a solution of esters **12c** and **12d** (13 mg, 0.026 mmol) and $Pd(PPh_3)_4$ (33 mg, 0.029 mmol) in DMF (260 μL, 0.1 M) was added tributyl(2-methoxyethynyl)stananne (**9**) (34 mg, 0.104 mmol). The reaction was stirred at 30 °C for 14 h. The reaction mixture was then filtered

through a Kimwipe plug with Et_2O (1.0 mL) (this removes a large excess of the undisolved $Pd(PPh_3)_4$) and is removed from the glovebox. Outside of the glovebox, the added Et_2O was removed by rotary evaporation, and the reaction was diluted with MeCN (15 mL). To this solution was then added pH 7 phosphate buffer (200 μL) and the reaction was stirred vigorously at 23 °C for two hours. Upon completion, MeCN was removed by rotary evaporation and the remaining aqueous solution was diluted with ethyl acetate (4 mL). This was then washed with water (3 x 1 mL) and the combined aqueous washes were back extracted with ethyl acetate (2 x 1 mL). All organics were pooled, dried with Na_2SO_4, and concentrated by rotary evaporation. The crude oil was purified by normal phase HPLC to yield 1.7 mg (20% yield) of transtaganolide C (**3**) and 0.9 mg (11% yield) of transtaganolide D (**4**) as white powders.

Transtaganolide C (3): $[\alpha]_D^{20}$ = +120.73 (*c* 0.42, $CHCl_3$, 96% ee); SFC conditions: 8.0% IPA, 2.5 mL/min, AD-H column, t_R(min): major = 12.19, minor = 13.15.

Transtaganolide D (4): $[\alpha]_D^{20}$ = –51.55 (*c* 0.17, $CHCl_3$, 92% ee); SFC conditions: 6.0% IPA, 2.5 mL/min, AD-H column, t_R(min): minor = 25.49, major = 29.77.

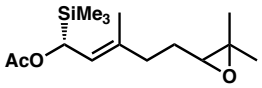
All other spectral data matches the literature. [2]



Allyl acetate SI-1. To a 0 °C solution of **16** (256 mg, 1.13 mmol) in pyridine (11 mL, 0.1M) was added acetic anhydride (534 μL, 5.65 mmol). The reaction was allowed to warm to 23 °C and was stirred for 6 hours. The solution was then diluted with ethyl acetate (30 mL) and quenched with saturated $NaHCO_3$ (10 mL). The organic layer was washed with saturated aqueous $CuSO_4$ (4 x 10 mL) until the dark blue color no longer persisted in the aqueous phase. This was followed by another saturated $NaHCO_3$ wash (10 mL), a brine wash (10 mL), and then drying over $MgSO_4$. Concentration by rotary evaporation gave a crude, colorless oil which could be taken on without further purification. Purification, if desired, was by column chromatography (ethyl acetate in hexanes 2⇒10% on SiO_2) to yield 260 mg (86% yield) of allyl acetate **SI-1**, as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.42 (d, *J* = 10.4 Hz, 1H), 5.16 (dm *J* = 10.4 Hz, 1H), 5.10–5.00 (m, 1H), 2.18–1.94 (m, 7H), 1.66 (s, 6H), 1.59 (s, 3H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 137.0, 131.7, 124.2, 121.7, 67.6, 40.0, 26.6, 25.9, 21.4, 17.9, 17.0, –3.7.

FTIR (Neat Film NaCl) 2962, 2927, 2856, 1737, 1443, 1368, 1290, 1248, 1237, 1158, 1109, 1014, 957, 842, 750 cm^{-1}; HRMS (EI) m/z calc'd for $C_{15}H_{29}O_2Si$ $[M]^+$: 268.1859, found 268.1863; $[\alpha]_D^{20}$ = +49.50 (*c* 1.00 in $CHCl_3$).

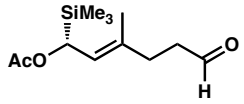


Epoxide SI-2. To a –78 °C solution of allyl acetate **SI-1** (260 mg, 0.97 mmol) in CH_2Cl_2 (10 mL, 0.1M) was added *m*-CPBA (max 77% by weight) (240 mg, 1.07 mmol). The

reaction was warmed to 0 °C and stirred for 30 minutes until complete as determined by TLC analysis. The reaction was quenched with 10% aqueous Na_2SO_3 (5 mL) at 0 °C. The organic layer is then separated from the aqueous and washed again with 10% Na_2SO_3 (5 mL). The combined aqueous layers were then combined and back extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with saturated $NaHCO_3$ (15 mL), brine (15 mL), and dried over $MgSO_4$. Concentration by rotary evaporation gave a crude oil, which was purified by column chromatography (ethyl acetate in hexanes 2%⇒10% on SiO_2) to yield 215 mg (78% yield) of **SI-2** as a colorless oil and a 1:1 mixture of diastereomers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (d, *J* = 10.3 Hz, 1H), 5.21 (dm, *J* = 10.3, 1H), 2.69 (td, *J* = 6.5, 5.3 Hz, 1H), 2.24–2.05 (m, 2H), 2.02 (s, 3H), 1.71–2.05 (m, 3H), 1.68–1.56 (m, 2H), 1.30–1.24 (m, 6H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.04, 171.02, 136.3, 136.2, 122.2, 122.1, 67.4, 64.1, 58.49, 58.48, 36.64, 36.56, 27.7, 27.5, 25.03, 25.00, 21.3, 18.9, 18.8, 17.1, 16.9, –3.6.

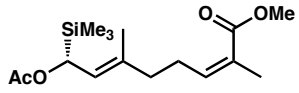
FTIR (Neat Film NaCl) 2960, 2928, 1736, 1732, 1446, 1377, 1369, 1323, 1291, 1248, 1238, 1123, 1046, 1015, 958, 842, 795, 751, 718 cm^{-1}; HRMS (ESI) m/z calc'd for $C_{15}H_{28}O_3SiNa$ $[M+Na]^+$: 307.1700, found 307.1706; $[\alpha]_D^{20}$ = +34.03 (*c* 1.00 in $CHCl_3$).



Aldehyde 23. To a solution of epoxide **SI-2** (244 mg, 0.86 mmol) in THF (8.6 mL, 0.1M) and water (4.8 mL, 0.18M) at 0 °C was added periodic acid (391 mg, 1.72 mmol). The reaction was stirred for 7 hours, diluted with Et_2O (25 mL), and quenched with saturated $NaHCO_3$ (10 mL). The aqueous layer was then separated from the organic and back extracted with Et_2O (2 x 10 mL). The combined organics were washed with brine (3 x 15 mL), dried over $MgSO_4$, and concentrated by rotary evaporation. Purification by column chromatography (ethyl acetate in hexanes 5%⇒25% on SiO_2) yielded 161 mg (77% yield) of aldehyde **23** as a colorless oil.

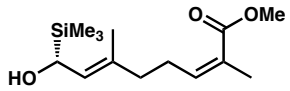
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.74 (t, *J* = 1.7 Hz, 1H), 5.37 (d, *J* = 10.3 Hz, 1H), 5.18 (dm, *J* = 10.3, 1H), 2.58–2.47 (m, 2H), 2.41–2.28 (m, 2H), 2.01 (s, 3H), 1.68 (s, 3H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.1, 171.0, 134.9, 122.7, 67.3, 42.2, 32.0, 21.3, 17.1, –3.7.

FTIR (Neat Film NaCl) 3432, 2958, 2902, 2823, 2720, 2479, 2113, 1732, 1415, 1368, 1291, 1248, 1142, 1115, 1046, 1016, 958, 842, 769, 752, 718 cm^{-1}; HRMS (ESI) m/z calc'd for $C_{12}H_{22}O_3SiNa$ $[M+Na]^+$: 265.1230, found 265.1232; $[\alpha]_D^{20}$ = +41.93 (*c* 1.00 in $CHCl_3$).

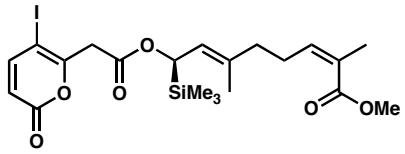


(*Z*)-Enone SI-3. To a –78 °C solution of KHMDS (35 mg, 0.18 mmol) in THF (2 mL) was added a solution of phosphonate reagent **24** (53.5 mg, 0.16 mmol) and 18-crown-6

(193.5 mg, 0.73 mmol) in THF (600 μL). After stirring the reaction mixture for 10 minutes at –78 °C, a solution of aldehyde **23** (35.5 mg, 0.15 mmol) in THF (600 μL) was added. This brings the total volume of THF to 3.2 mL, which is a 0.05M solution with respect to the Still-Gennari Reagent **24**. The reaction was stirred at –78 °C for 20 minutes and then quenched with a saturated NH_4Cl solution (1 mL) at –78 °C. After allowing the reaction mixture to warm to 23 °C, it was diluted with Et_2O (10 mL) and washed with saturated NH_4Cl (1 x 3 mL). Aqueous layers were combined and back extracted with Et_2O (2 x 3 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and concentrated by rotary evaporation. Purification was accomplished by column chromatography (ethyl acetate in hexanes 2%⇒10% on SiO_2) to yield 42.5 mg (93% yield) >25:1, *Z*:*E* of enone **SI-3** as a colorless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (tm, *J* = 7.2 Hz, 1H), 5.39 (d, *J* = 10.3 Hz, 1H), 5.17 (dm, *J* = 10.5 Hz, 1H), 3.72 (s, 3H), 2.58 (q, *J* = 7.5 Hz, 2H), 2.11 (t, *J* = 7.3 Hz, 2H), 2.02 (s, 3H), 1.88–1.85 (m, 3H), 1.67–1.66 (m, 3H), 0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 143.0, 136.3, 127.2, 122.3, 67.4, 51.3, 39.4, 27.9, 21.3, 20.8, 16.9, –3.7.
FTIR (Neat Film NaCl) 2954, 2928, 2855, 1722, 1649, 1453, 1434, 1368, 1289, 1248, 1238, 1199, 1131, 1104, 1085, 1015, 958, 842, 769, 751 cm^{-1}; HRMS (ESI) m/z calc'd for $C_{16}H_{28}O_4SiNa$ $[M+Na]^+$: 335.1649, found 335.1648; $[\alpha]_D^{20}$ = +49.43 (*c* 1.00 in $CHCl_3$).



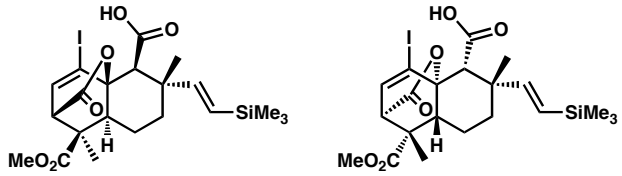
Alcohol 25. To a 23 °C solution of (*Z*)-enone **SI-3** (143 mg, 0.46 mmol) in MeOH (10 mL, 0.05M) was added K_2CO_3 (32 mg, 0.23 mmol). The resulting suspension was then stirred for 2.5 days until complete deprotection was observed by TLC. Following completion, the reaction was diluted with Et_2O (100 mL) and washed with water (2 x 75 mL). The combined aqueous washes were back extracted with Et_2O (3 x 75 mL). The organic phases were combined, washed with saturated brine (100 mL), dried over $MgSO_4$, and concentrated by rotary evaporation. Purification was accomplished by column chromatography (ethyl acetate in hexanes 5%⇒10% on SiO_2) to yield 96 mg (78%) of >25:1, *Z*:*E* of alcohol **25** as a colorless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.89 (tm, *J* = 7.3 Hz, 1H), 5.27 (dm, *J* = 10.1 Hz, 1H), 4.16 (d, *J* = 10.1 Hz, 1H), 3.71 (s, 3H), 2.63–2.52 (m, 2H), 2.11 (t, *J* = 7.3 Hz, 2H), 1.88–1.84 (m, 3H), 1.58 (d, *J* = 1.2 Hz, 3H), 0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 142.9, 134.3, 127.2, 126.9, 64.5, 51.4, 39.5, 28.0, 20.8, 16.7, –4.0.
FTIR (Neat Film NaCl) 3424, 2953, 2928, 2854, 1719, 1648, 1454, 1437, 1382, 1366, 1331, 1246, 1198, 1129, 1083, 1032, 978, 856, 841, 791, 749 cm^{-1}; HRMS (ESI) m/z calc'd for $C_{14}H_{26}O_3SiNa$ $[M+Na]^+$: 293.1543, found 293.1538; $[\alpha]_D^{20}$ = +56.83 (*c* 1.00 in $CHCl_3$).



Pyrone ester 26. To a 0 °C solution of alcohol **25** (297 mg, 1.10 mmol) in MeCN (11mL, 0.1M) were added sequentially pyrone acid **17** (339 mg, 1.21 mmol) and DCC (250 mg, 1.21 mmol). After 20 min at 0 °C the reaction was filtered through a plug of Celite, washing with MeCN. The filtrate was collected and concentrated by rotary evaporation. The crude oil was purified by column chromatography (ethyl acetate in hexanes 2%⇒10% on SiO_2) to yield 534 mg (91% yield) of pyrone ester **26** as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J = 9.7 Hz, 1H), 6.06 (d, J = 9.7 Hz, 1H), 5.88 (tm, J = 7.2 Hz, 1H), 5.41 (d, J = 10.4 Hz, 1H), 5.16 (dm, J = 10.4 Hz, 1H), 3.76 (s, 2H), 3.73 (s, 3H), 2.59 (tdm, J = 7.3, 7.2 Hz, 2H), 2.13 (t, J = 7.3 Hz, 2H), 1.87 (d, J = 1.4 Hz, 3H), 1.67 (d, J = 1.3 Hz, 3H), 0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 160.5, 158.5, 151.4, 142.9, 137.3, 127.2, 121.5, 116.1, 70.5, 69.6, 51.4, 43.1, 39.4, 27.9, 20.9, 16.9, –3.7.

FTIR (Neat Film NaCl) 2953, 2923, 2854, 1742, 1648, 1607, 1546, 1451, 1434, 1405, 1382, 1365, 1336, 1249, 1202, 1172, 1131, 1085, 1062, 1016, 960, 842, 764, 751, 729 cm^{-1}; HRMS (Multimode-ESI/APCI) m/z calc'd for $C_{21}H_{28}IO_6Si$ $[M–H]^-$: 531.0705, found 531.0712; $[\alpha]_D^{20}$ = +17.79 (*c* 1.00 in $CHCl_3$).



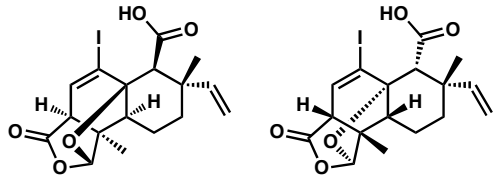
Vinyl silane 27 and 28. To a 23 °C solution of pyrone ester **17** (298 mg, 0.56 mmol) in toluene (2.8 mL, 0.2M) in a 500 mL sealed tube was added BSA (274 μL, 1.12 mmol) and NEt_3 (8 μL, 0.06 mmol). The reaction mixture was heated to 110 °C and stirred for 20 minutes. The mixture was then cooled to 23 °C and diluted with toluene (450 mL), leaving ample headspace in the sealed tube to allow for solvent expansion. The reaction mixture was then re-heated to 100 °C and stirred for 19 days, until completion, which was determined after monitoring by NMR. The reaction mixture was then cooled to 23 °C and 0.02% $HCl_{(aq)}$ (20 mL) was added and the mixture stirred vigorously for 1 minute. The organic phase was then separated and washed with 0.02% $HCl_{(aq)}$ (3 x 25 mL). Aqueous phases were then combined and back extracted with ethyl acetate (3 x 30 mL). The organic phases were combined, dried with Na_2SO_4, and concentrated by rotary evaporation. The crude oil was purified by column chromatography (ethyl acetate in hexanes with 0.1% acetic acid 5%⇒30% on SiO_2) to yield 186 mg (62% yield) of a 3:1 mixture of ICR/DA diastereomers **27** and **28** as a yellow solid. It is important to note that compounds **27** and **28**, and all subsequent compounds: **21**, **22**, **10a**, **10b**, **10c**, **10d**, **1**, and **2** have very poor solubility in most common organic solvents excluding ethyl acetate.

Therefore all transfers of products **27**, **28**, **21**, **22**, **10a**, **10b**, **10c**, **10d**, **1**, and **2** should be accomplished using ethyl acetate and vessels should be repeatedly washed.

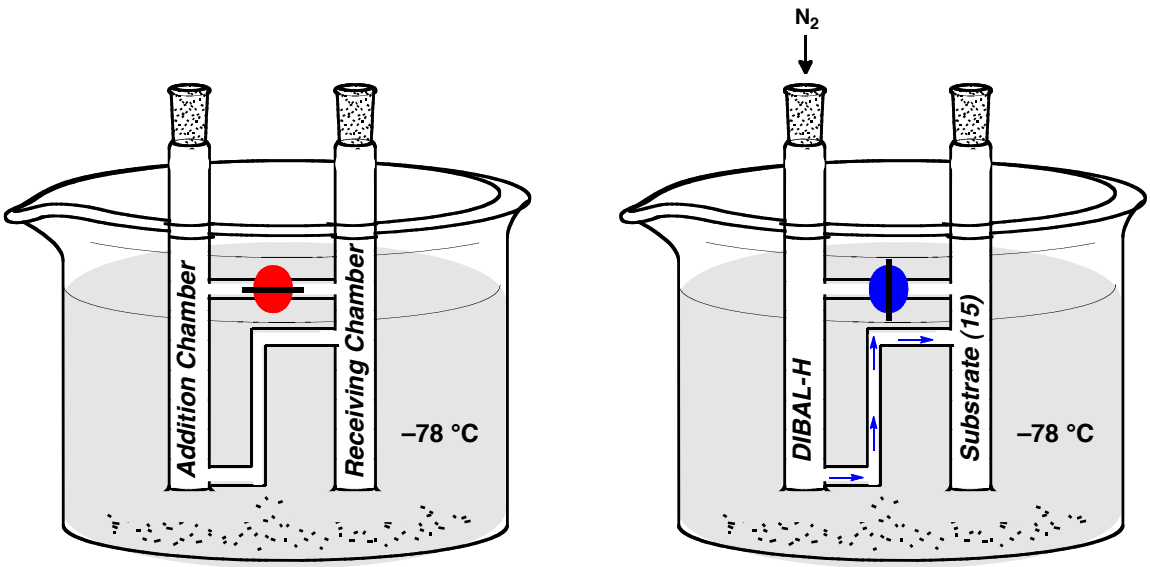
Major (27): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (d, *J* = 7.0 Hz, 1H), 6.09 (d, *J* = 18.8 Hz, 1H), 5.64 (d, *J* = 18.8 Hz, 1H), 3.74 (s, 3H), 3.36 (d, *J* = 7.0 Hz, 1H), 2.96 (s, 1H), 1.98–1.36 (m, 5H), 1.27 (s, 6H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 172.1, 168.9, 154.9, 139.8, 125.8, 99.8, 83.8, 59.2, 52.7, 51.5, 49.5, 49.2, 41.4, 37.9, 24.6, 20.8, 18.7, –1.0.

Minor (28): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (d, *J* = 6.9 Hz, 1H), 6.41 (d, *J* = 19.1 Hz, 1H), 5.64 (d, *J* = 19.1 Hz, 1H), 3.70 (s, 3H), 3.34 (d, *J* = 7.1 Hz, 1H), 2.91 (s, 1H), 1.98–1.36 (m, 5H), 1.30 (s, 3H), 1.25 (s, 3H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 171.9, 168.0, 147.5, 140.1, 128.1, 99.2, 83.9, 61.2, 52.5, 51.5, 49.6, 49.0, 40.6, 37.6, 29.6, 24.6, 20.7, –1.1.

FTIR (Neat Film NaCl) 3077, 2952, 1773, 1736, 1611, 1492, 1459, 1453, 1382, 1309, 1276, 1247, 1184, 1161, 1122, 1047, 1019, 989, 970, 935, 870, 838, 783, 754 cm^{-1}; HRMS (Multimode-ESI/APCI) m/z calc'd for $C_{21}H_{30}IO_6Si$ $[M+H]^+$: 533.0851, found 533.0847; $[\alpha]_D^{20}$ = +10.47 (*c* 1.00 in $CHCl_3$).



Acetal 10a and 10b. It is important to note that the selective single hydride reduction of the methyl esters of vinyl silanes **27** and **28** was only made possible using a glass cannula as it allows for the precise temperature control necessary to effect the transformation on such a complex molecule bearing many electrophilic carbonyl functionalities (Figure SI-5). A solution of vinyl silanes **27** and **28** (31 mg, 0.06 mmol) in toluene (600 μL, 0.1M) was stirred in the receiving chamber of the glass cannula at –78 °C (the entire glass cannula is placed in a –78 °C bath submerging both chambers and the cannula itself). A freshly made 1M solution of DIBAL-H (300 μL, 0.30 mmol) in toluene was added to the addition chamber of the glass cannula, further diluted with toluene (500 μL), and stirred at –78 °C. Once both solutions and the entire glass cannula were sufficiently cooled, the –78 °C solution of DIBAL-H was slowly added to vinyl silanes **27** and **28** dropwise. The reaction was stirred for 10 minutes and then slowly quenched by a –78 °C solution of AcOH (100 μL) in toluene (2 mL) via the addition chamber of the glass cannula. Once complete, the reaction vessel was removed from the –78 °C bath, allowed to warm to 23 °C, and then diluted with ethyl acetate (10 mL). The solution was washed with a 1% solution of AcOH in water (3 x 2 mL) and the aqueous phases were combined and back extracted with ethyl acetate (2 x 2 mL). All organic phases were pooled, dried over Na_2SO_4, and concentrated by rotary evaporation to give the desired aldehydes **21** and **22** as an orange-brown solid. **21** and **22** were used immediately in the following step without further purification.



Stopcock is open: material in addition chamber will not flow to the recieving chamber.

Stopcock is closed: material in addition chamber will flow to the recieving chamber when there is a difference in pressure.

Figure SI-5. Reaction schematic for the single hydride reduction of vinyl silanes **27** and **28** using a glass cannula.

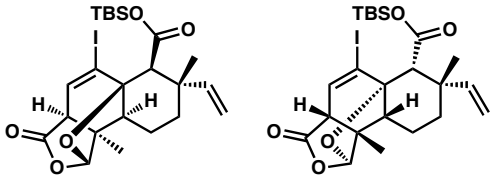
To a 23 °C solution of the crude aldehyde products (**21** and **22**) in MeCN (150 μL, 0.4M assuming quantitative yield from the reduction) was added aqueous HBF_4 (48% w/w, 100 μL, 0.78 mmol). The reaction was stirred at 23 °C for 8 hours and then diluted with ethyl acetate (5 mL). This was washed with pH 2–3 water (0.02% HCl solution) (3 x 1 mL), and the aqueous phases were back extracted with ethyl acetate (2 x 1 mL). All organics were combined, dried over Na_2SO_4, and concentrated by rotary evaporation. Purification was accomplished by column chromatography (ethyl acetate in hexanes with 0.1% acetic acid 5%⇒30% on SiO_2) to yield 15 mg (57% yield over 2 steps) of a 3:1 mixture of the reduced, cyclized, and desilylated diastereomers **10a** and **10b** as a yellow solid.

Major (10a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (d, J = 5.8 Hz, 1H), 6.03 (dd, J = 17.3, 10.8 Hz, 1H), 5.75 (s, 1H), 5.10 (d, J = 10.8 Hz, 1H), 5.04 (d, J = 17.4 Hz, 1H), 3.08 (d, J = 5.9 Hz, 1H), 2.92 (s, 1H), 2.21–2.14 (m, 1H), 1.97–1.38 (m, 4H), 1.36 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 169.5, 147.1, 136.1, 112.3, 108.9, 107.3, 87.1, 61.5, 54.7, 49.1, 48.8, 39.7, 36.2, 20.1, 18.8, 15.9.

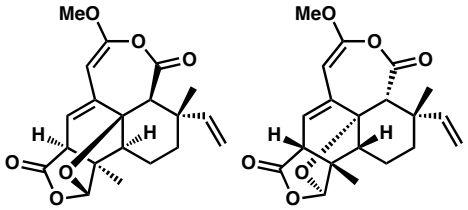
Minor (10b): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (d, J = 5.9 Hz, 1H), 6.07 (dd, J = 17.5, 11.1 Hz, 1H), 5.67 (s, 1H), 5.12 (d, J = 11.1 Hz, 1H), 5.08 (d, J = 17.5 Hz, 1H), 3.07 (d, J = 5.9 Hz, 1H), 2.88 (s, 1H), 2.21–2.14 (m, 1H), 1.97–1.38 (m, 4H), 1.36 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 169.7, 139.5, 136.3, 114.6, 108.8, 107.0, 87.1, 63.1, 54.7, 49.3, 48.8, 39.4, 36.3, 29.6, 20.0, 15.8.

FTIR (Neat Film NaCl) 3300, 3077, 3007, 2958, 2933, 2873, 1785, 1748, 1708, 1456, 1375, 1286, 1239, 1217, 1199, 1182, 1157, 1115, 1083, 1046, 1034, 992, 964, 957, 910,

895, 873, 829, 814, 796, 752 cm^{-1}; HRMS (Multimode-ESI/APCI) m/z calc'd for $C_{17}H_{20}IO_5$ $[M+H]^+$: 431.0350 found 431.0359; $[\alpha]_D^{20}$ = +18.71 (*c* 0.94 in $CHCl_3$).



TBS-ester 10c and 10d. To a 23 °C solution of acetals **10a** and **10b** (15 mg, 0.034 mmol) in DMF (600 μL, 0.055M) were added sequentially imidazole (14 mg, 0.21 mmol) and TBSCl (21 mg, 0.14 mmol). The reaction was stirred at 23 °C for 2 hours. The reaction mixture was then diluted with brine (2 mL) and extracted with ethyl acetate/hexane (1:1) (4 x 3 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (3 mL) and then with brine (2 x 3 mL). The combined organics were dried over Na_2SO_4 and concentrated by rotary evaporation. The crude oil was purified by column chromatography (ethyl acetate in hexane 10%⇒50% on SiO_2) to yield 12.5 mg (67% yield) of a 4:1 mixture of diasteromers **10c** and **10d** as a white solid.
Major (10c): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61 (d, *J* = 6.0 Hz, 1H), 6.00 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.68 (s, 1H), 4.99 (d, *J* = 10.7 Hz, 1H), 4.98 (d, *J* = 17.4 Hz, 1H), 2.98 (dd, *J* = 6.0, 0.8 Hz, 1H), 2.80 (s, 1H), 2.08–2.00 (m, 1H), 1.90–1.35 (m, 4H), 1.29 (s, 3H), 1.18 (s, 3H), 0.92 (s, 9H), 0.31 (s, 3H), 0.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 169.7, 149.2, 135.4, 110.9, 110.0, 109.8, 87.0, 61.1, 55.1, 49.5, 48.7, 40.0, 37.4, 25.7, 20.6, 18.2, 17.7, 16.0, –4.7.
Minor (10d): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61 (d, *J* = 6.1 Hz, 1H), 6.26 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.58 (s, 1H), 5.03 (dd, *J* = 11.0, 1.1 Hz, 1H), 4.97 (dd, *J* = 17.6, 1.1 Hz, 1H), 2.96 (dd, *J* = 6.1, 0.9 Hz, 1H), 2.72 (s, 1H), 2.08–2.00 (m, 1H), 1.90–1.35 (m, 4H), 1.32 (s, 3H), 1.26 (s, 3H), 0.93 (s, 9H), 0.31 (s, 3H), 0.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5, 169.9, 141.4, 135.6, 112.8, 109.9, 109.4, 87.0, 62.6, 55.1, 49.6, 48.9, 39.6, 37.7, 30.4, 25.6, 20.6, 17.6, 15.9, –4.8.
FTIR (Neat Film NaCl) 3083, 2930, 2857, 1784, 1716, 1638, 1601, 1471, 1463, 1413, 1390, 1362, 1338, 1317, 1282, 1250, 1235, 1222, 1196, 1183, 1160, 1144, 1115, 1084, 1049, 1036, 1000, 960, 942, 908, 895, 884, 868, 843, 828, 816, 787, 752 cm^{-1}; HRMS (Multimode-ESI/APCI) m/z calc'd for $C_{23}H_{34}IO_5Si$ $[M+H]^+$: 545.1215, found 545.1218; $[\alpha]_D^{20}$ = +49.09 (*c* 1.00 in $CHCl_3$).



Transtaganolides B and A (2 and 1). In a nitrogen filled glovebox, to a solution of TBS-esters **10c** and **10d** (9 mg, 0.0165 mmol) and $Pd(PPh_3)_4$ (21 mg, 0.018 mmol) in

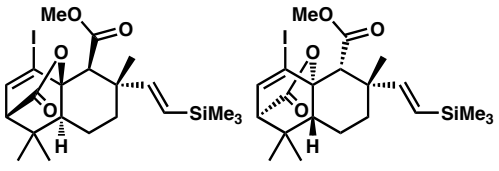
DMF (165 μL, 0.1M) was added tributyl(2-methoxyethynyl)stananne (**9**) (22 mg, 0.066 mmol). The heterogeneous reaction mixture was vigorously stirred at 31 °C for 7.5 h. The reaction mixture was then filtered through a Kimwipe with MeCN (1.5 mL) (this removes a large excess of the undisolved $Pd(PPh_3)_4$) and is removed from the glovebox. pH 7 phosphate buffer (75 μL) was added to the MeCN solution, which was then vigorously stirred for 36 hours. The reaction was then concentrated by rotary evaporation, as to remove some of the copious amounts of MeCN, and then diluted with ethyl acetate (2 mL). This was then washed with water (3 x 750 μL) and the combined aqueous washes were back extracted with ethyl acetate (2 x 750 μL). All organics were pooled, dried with Na_2SO_4, and concentrated by rotary evaporation. The crude oil was purified by normal phase HPLC to yield 1.5 mg (25% yield) of transtaganolide B (**2**) and 0.6 mg (10% yield) of transtaganolide A (**1**) as white powders.

Transtaganolide B (2): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.65 (t, 0.8 Hz, 1H), 5.58 (dd, *J* = 6.0, 1.1 Hz, 1H), 5.05 (dd, *J* = 17.4, 0.6 Hz, 1H), 5.02 (d, *J* = 10.8, 0.6 Hz, 1H), 4.96 (t, 0.8 Hz, 1H), 3.68 (s, 3H), 3.12 (dt, *J* = 6.0, 0.9 Hz, 1H), 3.08 (s, 1H), 1.94 (dd, *J* = 12.3, 6.3 Hz, 1H), 1.72 (ddt, *J* = 13.1, 6.3, 3.3 Hz, 1H), 1.63 (ddd, *J* = 13.1, 3.9, 2.7 Hz, 1H), 1.55 (s, 3H), 1.55–1.35 (m, 2H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 163.8, 154.5, 146.7, 144.2, 119.4, 112.7, 109.8, 87.7, 84.4, 56.5, 51.6, 49.8, 49.5, 48.8, 38.1, 37.0, 20.1, 19.4, 15.9.

FTIR (Neat Film NaCl) 2948, 2931, 2874, 2855, 1782, 1668, 1447, 1372, 1348, 1324, 1296, 1252, 1237, 1167, 1109, 1059, 1024, 999, 966, 912, 897, 843, 812, 736 cm^{-1}; HRMS (Multimode-ESI/APCI) m/z calc'd for $C_{20}H_{21}O_6$ $[M–H]^-$: 357.1344, found 357.1356; $[\alpha]_D^{20}$ = +207.93 (*c* 0.15, $CHCl_3$, 81% ee); SFC conditions: 25% IPA, 2.5 mL/min, AD-H column, t_R(min): major = 3.68, minor = 6.54.

Transtaganolide A (1): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (dd, *J* = 17.9, 11.1 Hz, 1H), 5.62 (s, 1H), 5.60 (dd, *J* = 5.9, 1.0 Hz, 1H), 5.12 (ddd, *J* = 11.1, 1.1, 0.6 Hz, 1H), 5.03 (dd, *J* = 17.9, 1.1 Hz, 1H), 4.98 (s, 1H), 3.70 (s, 3H), 3.11 (dt, *J* = 5.9, 0.8 Hz, 1H), 2.98 (s, 1H), 1.95 (dd, *J* = 12.3, 6.3 Hz, 1H), 1.83 (ddd, *J* = 12.9, 3.7, 2.6 Hz, 1H), 1.60–1.30 (m, 3H), 1.30 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 164.1, 154.5, 143.9, 143.8, 119.6, 111.8, 109.8, 87.6, 84.5, 56.5, 52.8, 51.6, 49.7, 48.8, 39.4, 38.3, 28.6, 20.1, 15.8.

FTIR (Neat Film NaCl) 2963, 2922, 2852, 1780, 1670, 1453, 1348, 1323, 1259, 1236, 1167, 1113, 1058, 1021m 999, 973, 959, 921, 840, 808, 731 cm^{-1}; HRMS (Multimode-ESI/APCI) m/z calc'd for $C_{20}H_{21}O_6$ $[M–H]^-$: 357.1344, found 357.1356; $[\alpha]_D^{20}$ = –98.76 (*c* 0.06, $CHCl_3$, 90% ee); SFC conditions: 30% IPA, 2.5 mL/min, AD-H column, t_R(min): minor = 3.20, major = 4.97.



Methyl esters 33 and SI-33: Diazomethane in a solution of diethyl ether is added dropwise to a 0.1M solution of the methyl esters **18** and **19** at 0 °C. This is done using

flame polished pipettes, glassware containing no ground glass joints, and open top to avoid detonation. The diazomethane is added until yellow color of diazomethane persists in the reaction solution. The reaction was then stirred for an additional 35 minutes, until lemon-lime color fades, and all unreacted diazomethane has evaporated into the well ventilated hood. The reaction was then concentrated by rotary evacuation and purified by preparatory HPLC, to separate diastereomers **33** and **SI-33**. The major diastereomer (**33**) was crystallized by slow evaporation from pentane in order to obtain crystals suitable for X-ray diffraction.

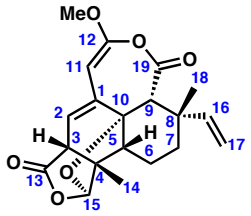
Major (33): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (d, *J* = 6.8 Hz, 1H), 6.10 (d, *J* = 18.9 Hz, 1H), 5.59 (d, *J* = 18.9 Hz, 1H), 3.61 (s, 3H), 2.97 (s, 1H), 2.94 (d, *J* = 6.8 Hz, 1H), 1.70–1.40 (m, 4H), 1.34 (dd, *J* = 12.0, 5.3 Hz, 1H), 1.23 (s, 3H), 1.08 (s, 3H), 1.00 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 169.3, 156.1, 140.3, 124.5, 98.0, 84.7, 59.0, 56.9, 51.2, 48.3, 41.5, 38.2, 37.0, 30.0, 24.7, 20.9, 18.4, –0.9.

FTIR (Neat Film NaCl) 2953, 2923, 2848, 1746, 1612, 1464, 1454, 1392, 1386, 1365, 1352, 1302, 1246, 1209, 1196, 1167, 1141, 1052, 1011, 993, 976, 965, 939, 868, 838, 796, 756 cm^{-1}; HRMS (Multimode-ESI/APCI) m/z calc'd for $C_{21}H_{32}IO_4Si$ $[M+H]^+$: 503.1109 found 503.1113; $[\alpha]_D^{20}$ = +34.50 (*c* 0.24 in $CHCl_3$); MP: 125–130 ºC.

Minor (SI-33): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (d, *J* = 6.8 Hz, 1H), 6.48 (d, *J* = 19.2 Hz, 1H), 5.57 (d, *J* = 19.2 Hz, 1H), 3.68 (s, 3H), 2.90 (d, *J* = 6.8 Hz, 1H), 2.87 (s, 1H), 1.96 (dt, *J* = 13.7, 3.4 Hz, 1H), 1.66–1.51 (m, 2H), 1.41 (td, *J* = 13.5, 3.4 Hz, 1H), 1.34 (dd, *J* = 12.6, 5.0 Hz, 1H), 1.27 (s, 3H), 1.02 (s, 3H), 0.97 (s, 3H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 169.6, 148.9, 140.4, 126.6, 110.1, 97.7, 84.5, 61.1, 57.0, 51.7, 48.3, 40.8, 38.3, 37.2, 30.0, 24.6, 20.9, –1.1.

FTIR (Neat Film NaCl) 2952, 2893, 1760, 1745, 1608, 1455, 1435, 1394, 1372, 1354, 1304, 1246, 1224, 1190, 1168, 1149, 1137, 1102, 1047, 1012, 994, 955, 869, 838, 799, 755, 737, 727 cm^{-1}; HRMS (Multimode-ESI/APCI) m/z calc'd for $C_{21}H_{32}IO_4Si$ $[M+H]^+$: 503.1109 found 503.1119; $[\alpha]_D^{20}$ = –82.77 (*c* 0.37 in $CHCl_3$).

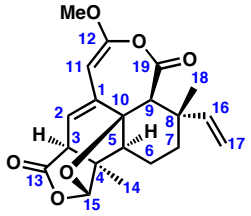
III. Comparison of Spectral Data for Synthetic and Reported Transaganolide A (1) and B (2)



transtaganolide A (1)

Table SI-1. Comparison of ^{1}H NMR data for synthetic and reported natural[3] transtaganolide A (**1**).

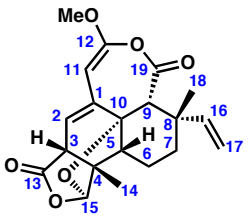
Assignment	Synthetic 1 (ppm)	Multiplicity, *J* (Hz)	Natural 1 (ppm)	Multiplicity, *J* (Hz)
C1	—	—	—	—
C2	5.60	dd, 5.9, 1.0	5.60	dd, 5.9, 1.1
C3	3.11	dt, 5.9, 0.8	3.11	d, 6.0
C4	—	—	—	—
C5	1.95	d, 12.3, 6.3	1.96	d, 12.1, 6.2
C6	1.60–1.30	m	1.60	dddd, 13.3, 6.2, 2.7, 2.2
	1.60–1.30	m	1.47	dddd, 13.3, 13.3, 12.3, 2.3
C7	1.60–1.30	m	1.39	ddd, 13.3, 13.3, 2.7
	1.83	ddd, 12.9, 3.7, 2.6	1.82	ddd, 12.7, 3.7, 2.2
C8	—	—	—	—
C9	2.98	s	2.99	s
C10	—	—	—	—
C11	4.98	s	4.99	br s
C12	—	—	—	—
C13	—	—	—	—
C14	1.30	s	1.30	s
C15	5.62	s	5.61	s
C16	6.90	dd, 17.9, 11.1	6.89	dd, 17.9, 11.2
C17	5.12	ddd, 11.1, 1.1, 0.6	5.11	ddt, 11.1, 1.1, 0.6
	5.03	dd, 17.9 1.1	5.03	dd, 17.8, 1.1
C18	1.22	s	1.22	s
C19	—	—	—	—
OMe	3.70	s	3.70	s



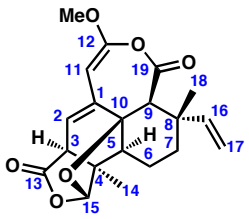
transtaganolide B (2)

Table SI-2. Comparison of ^{1}H NMR data for synthetic and reported natural[3] transtaganolide B (**2**).

Assignment	Synthetic 1 (ppm)	Multiplicity, *J* (Hz)	Natural 1 (ppm)	Multiplicity, *J* (Hz)
C1	—	—	—	—
C2	5.58	dd, 6.0, 1.1	5.58	dd, 6.0 1.1
C3	3.12	dt, 6.0, 0.9	3.12	dt, 6.0, 0.9
C4	—	—	—	—
C5	1.94	dd, 12.3, 6.3	1.95	dd, 12.1, 6.3
C6	1.72	ddt, 13.1, 6.3, 3.3	1.73	dddd, 12.9, 6.2, 3.7, 2.5
	1.55–1.35	m	1.51	dddd, 13.0, 13.0, 13.0, 2.4
C7	1.55–1.35	m	1.43	ddd, 13.3, 11.9, 2.3
	1.63	ddd, 13.1, 3.9, 2.7	1.63	ddd, 13.3, 3.7, 2.3
C8	—	—	—	—
C9	3.08	s	3.09	s
C10	—	—	—	—
C11	4.96	t, 0.8	4.97	t, 0.8
C12	—	—	—	—
C13	—	—	—	—
C14	1.33	s	1.33	s
C15	5.65	t, 0.8	5.66	t, 0.7
C16	5.80	dd, 17.4, 10.8	5.81	dd, 17.4, 10.8
C17	5.05	dd, 17.4, 0.6	5.09	dd, 10.8, 0.7
	5.02	dd, 10.8, 0.6	5.06	dd, 17.4, 0.7
C18	1.55	s	1.55	s
C19	—	—	—	—
OMe	3.68	s	3.68	s



transtaganolide A (1)



transtaganolide B (2)

Table SI-3. Comparison of ^{13}C NMR data for synthetic and reported natural[3] transtaganolides A and B (**1** and **2**).

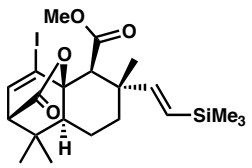
Assignment	Synthetic 1 (ppm)	Natural 1 (ppm)	Synthetic 2 (ppm)	Natural 2 (ppm)
C1	143.8	143.7	144.2	144.0
C2	119.6	119.4	119.4	119.2
C3	51.6	51.3	51.6	51.4
C4	48.8	48.6	48.8	48.6
C5	49.7	49.4	49.5	49.3
C6	20.1	19.9	19.4	19.2
C7	39.4	39.1	37.0	36.8
C8	38.3	38.1	38.1	37.9
C9	52.8	52.5	49.8	49.6
C10	87.6	87.5	87.7	87.5
C11	84.5	84.1	84.4	84.2
C12	154.5	154.4	154.5	154.3
C13	175.6	175.5	175.6	175.5
C14	15.8	15.6	15.9	15.7
C15	109.8	109.6	109.8	109.6
C16	143.9	143.7	146.7	146.5
C17	111.8	111.5	112.7	112.5
C18	28.6	28.3	20.1	19.9
C19	164.1	164.0	163.8	163.7
OMe	56.5	56.3	56.5	56.3

[1] W. Zeng, R. Fröhlich, D. Hoppe, *Tetrahedron* **2005**, *61*, 3281–3287.

[2] H. M. Nelson, K. Murakami, S. C. Virgil, B. M. Stoltz, *Angew. Chem. Int. Ed.* **2011**, *50*, 3688–3691.

[3] A. Saouf, F. M. Guerra, J. J. Rubal, F. J. Moreno-Dorado, M. Akssira, F. Mellouki, M. Lopez, A. J. Pujadas, Z. D. Jorge, G. M. Massanet, *Org. Lett.* **2005**, *7*, 881–884.

IV. Crystal Structure Analysis of:



33

By Larry Henling 128 Beckman ext. 2735
e-mail: xray@caltech.edu

Contents

Table SI-4. Crystal data
Table SI-5. Atomic Coordinates
Table SI-6. Full bond distances and angles
Table SI-7. Anisotropic displacement parameters
Table SI-8. Hydrogen atomic coordinates
Table SI-9. Observed and calculated structure factors (available upon request)

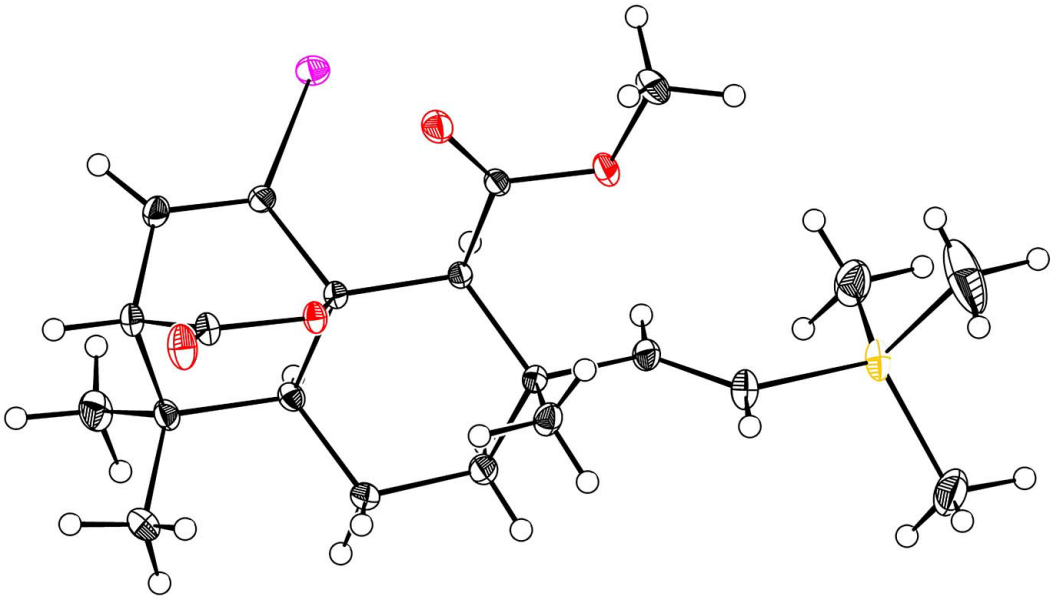


Figure SI-6. Ortep diagram of **33**. The crystallographic data have been deposited in the Cambridge Database (CCDC) and has been placed on hold pending further instructions.

Table SI-4. Crystal data and structure analysis details for 33.

Empirical formula	C21 H31 I O4 Si
Formula weight	502.45
Crystallization solvent	Hexanes/Pentane
Crystal shape	block
Crystal color	colorless
Crystal size	0.28 x 0.3 x 0.38 mm

Data Collection

Preliminary photograph(s)	rotation
Type of diffractometer	Bruker APEX-II CCD
Wavelength	0.71073 ≈ MoK
Data collection temperature	100 K

Theta range for 9418 reflections used		
in lattice determination	2.69 to 49.27∞	
Unit cell dimensions	a = 7.8106(6) ≈	α= 90∞
	b = 9.9557(9) ≈	β= 90∞
	c = 29.925(3) ≈	γ = 90∞
Volume	2326.9(3) ≈^{3}	
Z	4	
Crystal system	orthorhombic	
Space group	P 21 21 21 (# 19)	
Density (calculated)	1.434 g/cm^3	
F(000)	1024	
Theta range for data collection	2.2 to 51.0∞	
Completeness to theta = 25.00∞	99.9%	
Index ranges	-16 ≤ h ≤ 8, -21 ≤ k ≤ 21, -61 ≤ l ≤ 65	
Data collection scan type	and scans	
Reflections collected	91039	
Independent reflections	24693 [R_{int}= 0.0329]	
Reflections > 2σ(I)	22910	
Average σ(I)/(net I)	0.0301	
Absorption coefficient	1.45 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8799 and 0.8128	

Structure Solution and Refinement

Primary solution method	dual
Secondary solution method	difmap
Hydrogen placement	geom
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	24693 / 0 / 368

Treatment of hydrogen atoms	refall
Goodness-of-fit on F^2	1.71
Final R indices [I>2σ(I), 22910 reflections]	R1 = 0.0322, wR2 = 0.0520
R indices (all data)	R1 = 0.0364, wR2 = 0.0525
Type of weighting scheme used	calc
Weighting scheme used	calc w=1/[^2^(Fo^2^)]
Max shift/error	0.002
Average shift/error	0.000
Absolute structure parameter	-0.001(5)
Largest diff. peak and hole	2.58 and -2.43 e∑≈$^{-3}$

Programs Used

Cell refinement	SAINT V8.18C (Bruker-AXS, 2007)
Data collection	APEX2 2012.2-0 (Bruker-AXS, 2007)
Data reduction	SAINT V8.18C (Bruker-AXS, 2007)
Structure solution	SHELXS-97 (Sheldrick, 1990)
Structure refinement	SHELXL-97 (Sheldrick, 1997)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

Table SI-5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 33. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
I(1)	3229(1)	3273(1)	1007(1)	15(1)
Si(1)	8286(1)	9598(1)	296(1)	18(1)
O(1)	5867(1)	5072(1)	2118(1)	11(1)
O(2)	5592(1)	4487(1)	2829(1)	19(1)

O(3)	3205(1)	6242(1)	1658(1)	17(1)
O(4)	4368(1)	7639(1)	1154(1)	18(1)
C(1)	6046(1)	4527(1)	1664(1)	10(1)
C(2)	6004(1)	5727(1)	1341(1)	10(1)
C(3)	7647(1)	6616(1)	1326(1)	12(1)
C(4)	9209(1)	5673(1)	1298(1)	17(1)
C(5)	9286(1)	4665(1)	1680(1)	15(1)
C(6)	7759(1)	3724(1)	1662(1)	12(1)
C(7)	7701(1)	2636(1)	2044(1)	13(1)
C(8)	5895(1)	2726(1)	2272(1)	13(1)
C(9)	4551(1)	2554(1)	1916(1)	14(1)
C(10)	4638(1)	3483(1)	1598(1)	12(1)
C(11)	5751(1)	4138(1)	2445(1)	12(1)
C(12)	4363(1)	6542(1)	1412(1)	11(1)
C(13)	2917(1)	8524(1)	1196(1)	21(1)
C(14)	7682(1)	7423(1)	893(1)	14(1)
C(15)	8219(1)	8682(1)	840(1)	17(1)
C(16)	7633(2)	8455(1)	-168(1)	29(1)
C(17)	6799(3)	11047(2)	328(1)	51(1)
C(18)	10497(2)	10244(2)	195(1)	31(1)
C(19)	7776(1)	7534(1)	1736(1)	15(1)
C(20)	9053(1)	2839(1)	2411(1)	20(1)
C(21)	7953(1)	1234(1)	1846(1)	20(1)

Table SI-6. **Bond lengths [Å] and angles [°] for 33.**

I(1)-C(10)	2.0931(7)
Si(1)-C(15)	1.8650(8)
Si(1)-C(16)	1.8677(12)
Si(1)-C(17)	1.8543(14)
Si(1)-C(18)	1.8672(13)
O(1)-C(1)	1.4684(9)
O(1)-C(11)	1.3539(10)
O(2)-C(11)	1.2063(11)
O(3)-C(12)	1.2049(10)
O(4)-C(12)	1.3363(10)
O(4)-C(13)	1.4404(11)
C(1)-C(2)	1.5377(11)
C(1)-C(6)	1.5580(11)
C(1)-C(10)	1.5261(11)
C(2)-H(2)	1.015(14)
C(2)-C(3)	1.5596(10)
C(2)-C(12)	1.5307(10)
C(3)-C(4)	1.5419(12)
C(3)-C(14)	1.5258(11)
C(3)-C(19)	1.5320(12)
C(4)-H(4A)	1.008(15)
C(4)-H(4B)	0.875(17)
C(4)-C(5)	1.5223(12)
C(5)-H(5A)	1.052(15)
C(5)-H(5B)	0.959(14)

C(5)-C(6)	1.5178(12)
C(6)-H(6)	1.030(13)
C(6)-C(7)	1.5739(12)
C(7)-C(8)	1.5698(11)
C(7)-C(20)	1.5367(12)
C(7)-C(21)	1.5297(13)
C(8)-H(8)	1.004(16)
C(8)-C(9)	1.5052(12)
C(8)-C(11)	1.5022(12)
C(9)-H(9)	0.930(16)
C(9)-C(10)	1.3303(11)
C(13)-H(13A)	0.951(16)
C(13)-H(13B)	0.993(14)
C(13)-H(13C)	0.904(18)
C(14)-H(14)	0.928(14)
C(14)-C(15)	1.3312(13)
C(15)-H(15)	0.997(18)
C(16)-H(16A)	0.915(17)
C(16)-H(16B)	1.04(2)
C(16)-H(16C)	1.020(18)
C(17)-H(17A)	0.80(3)
C(17)-H(17B)	1.01(2)
C(17)-H(17C)	0.99(2)
C(18)-H(18A)	1.020(18)
C(18)-H(18B)	0.93(2)
C(18)-H(18C)	0.88(2)
C(19)-H(19A)	0.904(15)
C(19)-H(19B)	0.952(15)
C(19)-H(19C)	0.886(16)
C(20)-H(20A)	0.920(16)
C(20)-H(20B)	0.950(17)
C(20)-H(20C)	0.924(16)
C(21)-H(21A)	1.003(14)
C(21)-H(21B)	0.889(18)
C(21)-H(21C)	0.987(16)
C(15)-Si(1)-C(16)	110.06(5)
C(15)-Si(1)-C(18)	109.60(5)
C(17)-Si(1)-C(15)	108.59(6)
C(17)-Si(1)-C(16)	109.91(9)
C(17)-Si(1)-C(18)	108.64(10)
C(18)-Si(1)-C(16)	110.01(6)
C(11)-O(1)-C(1)	114.95(6)
C(12)-O(4)-C(13)	116.59(7)
O(1)-C(1)-C(2)	106.94(6)
O(1)-C(1)-C(6)	105.89(6)
O(1)-C(1)-C(10)	107.66(6)
C(2)-C(1)-C(6)	114.54(6)
C(10)-C(1)-C(2)	115.60(6)
C(10)-C(1)-C(6)	105.64(6)
C(1)-C(2)-H(2)	105.4(8)
C(1)-C(2)-C(3)	116.17(6)
C(3)-C(2)-H(2)	107.3(8)
C(12)-C(2)-C(1)	110.08(6)
C(12)-C(2)-H(2)	103.7(8)
C(12)-C(2)-C(3)	113.09(6)
C(4)-C(3)-C(2)	107.88(7)
C(14)-C(3)-C(2)	109.73(6)
C(14)-C(3)-C(4)	105.03(6)

C(14)-C(3)-C(19)	111.41(7)
C(19)-C(3)-C(2)	111.72(6)
C(19)-C(3)-C(4)	110.80(7)
C(3)-C(4)-H(4A)	109.0(8)
C(3)-C(4)-H(4B)	108.2(11)
H(4A)-C(4)-H(4B)	110.6(13)
C(5)-C(4)-C(3)	113.04(7)
C(5)-C(4)-H(4A)	109.2(8)
C(5)-C(4)-H(4B)	106.8(10)
C(4)-C(5)-H(5A)	110.4(8)
C(4)-C(5)-H(5B)	106.8(8)
H(5A)-C(5)-H(5B)	109.1(12)
C(6)-C(5)-C(4)	110.45(7)
C(6)-C(5)-H(5A)	111.9(8)
C(6)-C(5)-H(5B)	108.1(8)
C(1)-C(6)-H(6)	106.3(7)
C(1)-C(6)-C(7)	109.03(6)
C(5)-C(6)-C(1)	111.02(7)
C(5)-C(6)-H(6)	108.4(7)
C(5)-C(6)-C(7)	114.99(7)
C(7)-C(6)-H(6)	106.6(7)
C(8)-C(7)-C(6)	107.59(6)
C(20)-C(7)-C(6)	114.06(7)
C(20)-C(7)-C(8)	107.40(7)
C(21)-C(7)-C(6)	110.09(7)
C(21)-C(7)-C(8)	109.68(7)
C(21)-C(7)-C(20)	107.94(7)
C(7)-C(8)-H(8)	110.6(9)
C(9)-C(8)-C(7)	108.20(6)
C(9)-C(8)-H(8)	114.9(9)
C(11)-C(8)-C(7)	105.71(7)
C(11)-C(8)-H(8)	109.7(9)
C(11)-C(8)-C(9)	107.34(7)
C(8)-C(9)-H(9)	119.6(9)
C(10)-C(9)-C(8)	113.10(7)
C(10)-C(9)-H(9)	127.0(9)
C(1)-C(10)-I(1)	123.83(5)
C(9)-C(10)-I(1)	120.64(6)
C(9)-C(10)-C(1)	114.63(7)
O(1)-C(11)-C(8)	112.82(6)
O(2)-C(11)-O(1)	119.90(8)
O(2)-C(11)-C(8)	127.25(8)
O(3)-C(12)-O(4)	123.87(7)
O(3)-C(12)-C(2)	125.54(7)
O(4)-C(12)-C(2)	110.58(6)
O(4)-C(13)-H(13A)	107.9(10)
O(4)-C(13)-H(13B)	110.3(8)
O(4)-C(13)-H(13C)	110.2(12)
H(13A)-C(13)-H(13B)	109.1(12)
H(13A)-C(13)-H(13C)	114.6(15)
H(13B)-C(13)-H(13C)	104.8(14)
C(3)-C(14)-H(14)	113.4(9)
C(15)-C(14)-C(3)	127.14(8)
C(15)-C(14)-H(14)	119.3(9)
Si(1)-C(15)-H(15)	116.0(10)
C(14)-C(15)-Si(1)	125.05(7)
C(14)-C(15)-H(15)	118.5(10)
Si(1)-C(16)-H(16A)	108.5(10)

Si(1)-C(16)-H(16B)	110.7(10)
Si(1)-C(16)-H(16C)	113.9(11)
H(16A)-C(16)-H(16B)	106.6(15)
H(16A)-C(16)-H(16C)	112.0(15)
H(16B)-C(16)-H(16C)	104.8(15)
Si(1)-C(17)-H(17A)	105(2)
Si(1)-C(17)-H(17B)	110.7(13)
Si(1)-C(17)-H(17C)	103.4(14)
H(17A)-C(17)-H(17B)	103(2)
H(17A)-C(17)-H(17C)	126(2)
H(17B)-C(17)-H(17C)	108.5(18)
Si(1)-C(18)-H(18A)	111.1(11)
Si(1)-C(18)-H(18B)	109.9(13)
Si(1)-C(18)-H(18C)	104.1(16)
H(18A)-C(18)-H(18B)	109.8(16)
H(18A)-C(18)-H(18C)	108.5(18)
H(18B)-C(18)-H(18C)	113(2)
C(3)-C(19)-H(19A)	112.9(10)
C(3)-C(19)-H(19B)	112.8(9)
C(3)-C(19)-H(19C)	110.1(9)
H(19A)-C(19)-H(19B)	104.8(13)
H(19A)-C(19)-H(19C)	105.1(13)
H(19B)-C(19)-H(19C)	110.7(13)
C(7)-C(20)-H(20A)	107.2(10)
C(7)-C(20)-H(20B)	110.3(10)
C(7)-C(20)-H(20C)	110.6(9)
H(20A)-C(20)-H(20B)	107.5(13)
H(20A)-C(20)-H(20C)	111.0(14)
H(20B)-C(20)-H(20C)	110.3(14)
C(7)-C(21)-H(21A)	107.9(8)
C(7)-C(21)-H(21B)	114.7(12)
C(7)-C(21)-H(21C)	113.7(9)
H(21A)-C(21)-H(21B)	110.7(12)
H(21A)-C(21)-H(21C)	109.6(12)
H(21B)-C(21)-H(21C)	100.0(14)

Symmetry transformations used to generate equivalent atoms:

Table SI-7. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 33. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	153(1)	162(1)	141(1)	-20(1)	-36(1)	-19(1)
Si(1)	248(1)	130(1)	151(1)	45(1)	40(1)	16(1)
O(1)	155(2)	82(2)	85(2)	0(2)	5(2)	6(2)
O(2)	318(4)	150(3)	106(2)	8(2)	23(2)	13(2)
O(3)	139(2)	179(3)	181(2)	39(2)	29(2)	33(2)
O(4)	154(2)	162(3)	233(3)	93(2)	1(2)	34(2)
C(1)	116(2)	85(3)	86(2)	1(2)	-1(2)	3(2)
C(2)	110(2)	91(3)	94(2)	6(2)	-6(2)	-1(2)
C(3)	120(2)	109(3)	117(3)	16(2)	-6(2)	-15(2)
C(4)	117(3)	181(4)	200(4)	68(3)	24(2)	9(2)
C(5)	106(3)	166(4)	192(3)	48(3)	-7(2)	8(2)
C(6)	119(2)	112(3)	115(3)	6(2)	5(2)	24(2)

C(7)	148(3)	98(3)	148(3)	17(2)	-11(2)	20(2)
C(8)	167(3)	90(3)	131(3)	22(2)	-1(2)	2(2)
C(9)	149(3)	98(3)	160(3)	5(2)	2(2)	-15(2)
C(10)	115(2)	103(3)	128(3)	-4(2)	-16(2)	-9(2)
C(11)	161(3)	103(3)	108(3)	14(2)	5(2)	7(2)
C(12)	118(2)	99(3)	118(3)	7(2)	-19(2)	9(2)
C(13)	192(4)	165(4)	271(4)	34(3)	-35(3)	58(3)
C(14)	151(3)	149(3)	115(3)	23(2)	9(2)	-11(2)
C(15)	237(3)	132(3)	147(3)	26(2)	28(3)	-6(3)
C(16)	380(6)	294(6)	191(4)	60(4)	-41(3)	-109(4)
C(17)	732(12)	401(8)	403(8)	181(7)	221(8)	366(9)
C(18)	363(6)	296(6)	274(5)	104(5)	-16(4)	-138(5)
C(19)	190(3)	143(3)	124(3)	8(3)	-24(2)	-49(3)
C(20)	189(3)	211(4)	188(4)	57(3)	-58(3)	5(3)
C(21)	238(4)	119(3)	256(4)	-9(3)	21(3)	51(3)

Table SI-8. Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$x 10^3) for 33.

	x	y	z	U_{iso}
H(2)	585(2)	532(1)	103(1)	16(3)
H(4A)	917(2)	517(1)	100(1)	18(3)
H(4B)	1014(2)	616(2)	132(1)	23(4)
H(5A)	937(2)	517(2)	199(1)	20(3)
H(5B)	1030(2)	414(1)	164(1)	11(3)
H(6)	779(2)	321(1)	136(1)	10(3)
H(8)	581(2)	208(2)	253(1)	24(4)
H(9)	384(2)	181(2)	192(1)	22(3)
H(13A)	197(2)	811(2)	105(1)	28(4)
H(13B)	316(2)	940(1)	105(1)	16(3)
H(13C)	273(2)	872(2)	149(1)	38(5)
H(14)	735(2)	693(2)	64(1)	17(3)
H(15)	848(2)	923(2)	111(1)	37(5)
H(16A)	657(2)	812(2)	-11(1)	30(4)
H(16B)	845(2)	763(2)	-19(1)	40(5)
H(16C)	768(2)	889(2)	-48(1)	42(5)
H(17A)	587(4)	1072(3)	33(1)	80(10)
H(17B)	680(3)	1156(2)	4(1)	65(6)
H(17C)	731(3)	1162(2)	56(1)	59(6)
H(18A)	1056(2)	1077(2)	-10(1)	37(5)
H(18B)	1127(3)	953(2)	19(1)	48(6)
H(18C)	1068(3)	1080(2)	42(1)	58(6)
H(19A)	875(2)	802(2)	174(1)	22(4)
H(19B)	777(2)	705(2)	201(1)	23(4)
H(19C)	694(2)	814(2)	173(1)	21(3)
H(20A)	885(2)	220(2)	263(1)	23(4)
H(20B)	892(2)	370(2)	255(1)	25(4)
H(20C)	1014(2)	275(2)	229(1)	24(4)
H(21A)	910(2)	121(2)	170(1)	14(3)
H(21B)	714(2)	98(2)	166(1)	31(4)
H(21C)	788(2)	50(2)	207(1)	25(4)

V. CD Data

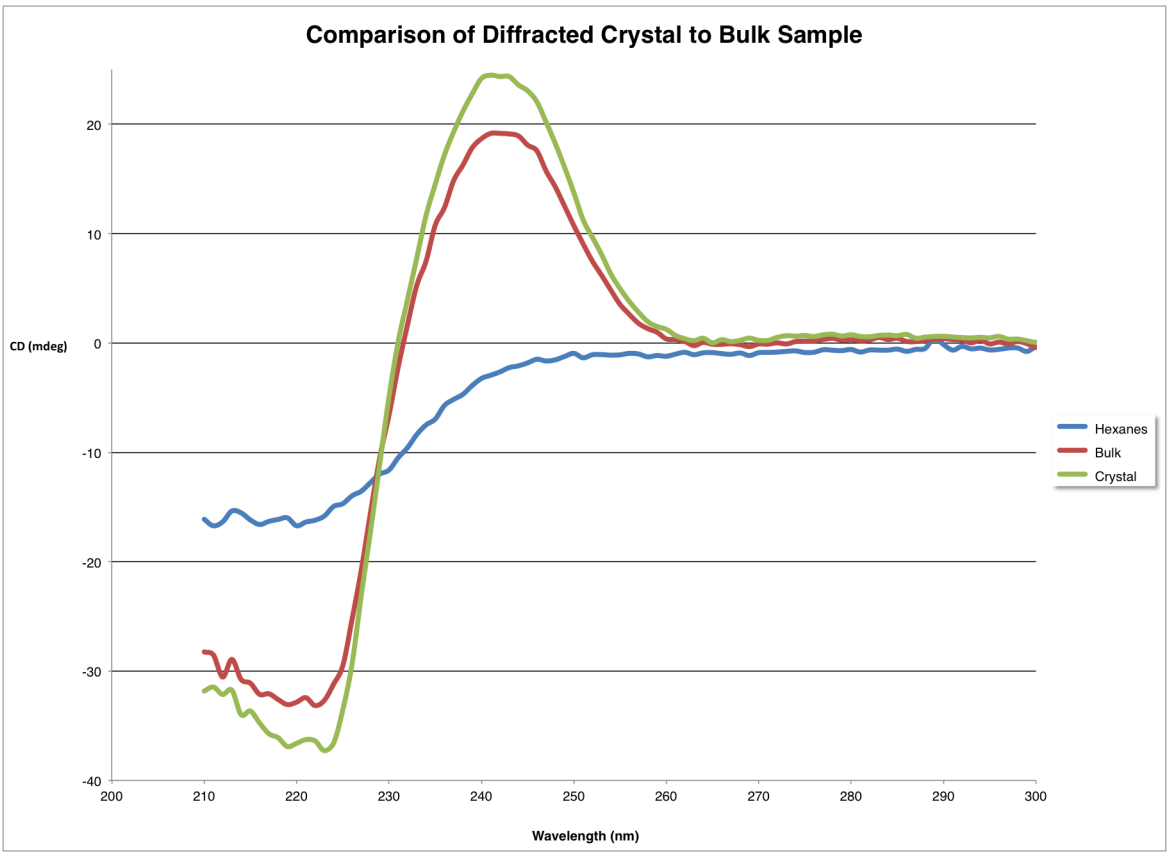


Figure SI-7. The CD spectra of crystal **33** (in green) and the CD spectra of the bulk material which crystal **33** was obtained (in red). Since crystal **33** was grown from 90% ee material it was possible that crystal **33** could have been the crystallized minor enantiomer. Figure SI-7 demonstrates that the CD spectra of the bulk material and crystal **33** are quite similar and therefore confirms that crystal **33** is representative of the major enantiomer.

VI. Spectra

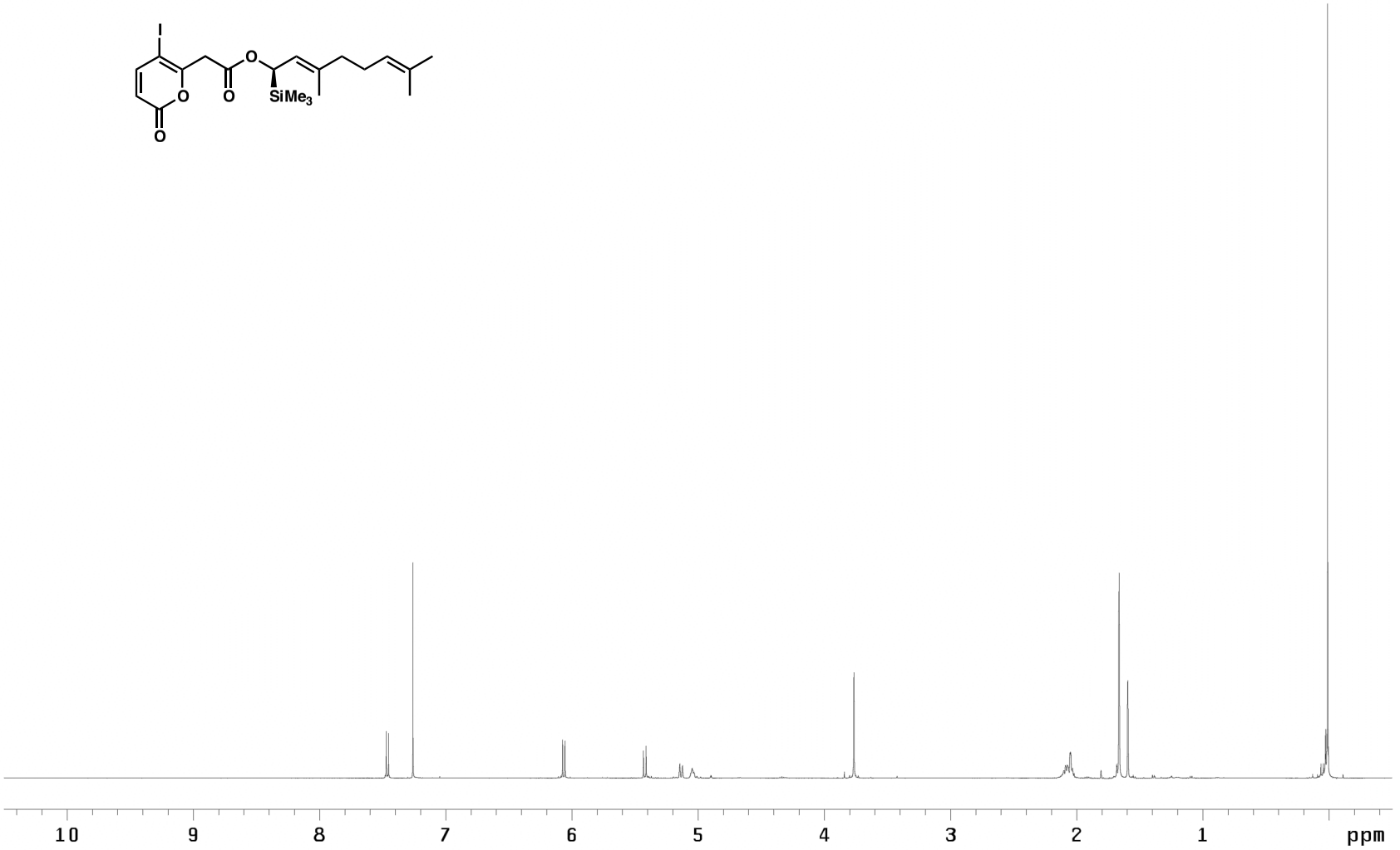


Figure SI-8A ^{1}H NMR (500 MHz, $CDCl_3$) of compound **13**

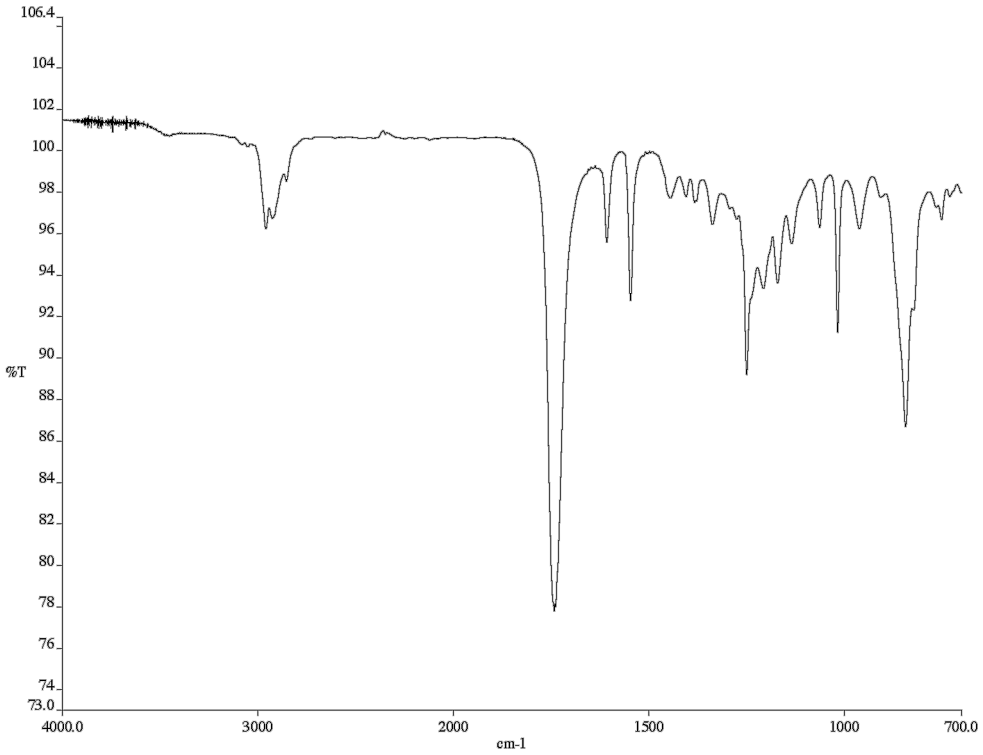


Figure SI-8B Infrared spectrum (thin film/NaCl) of compound **13**

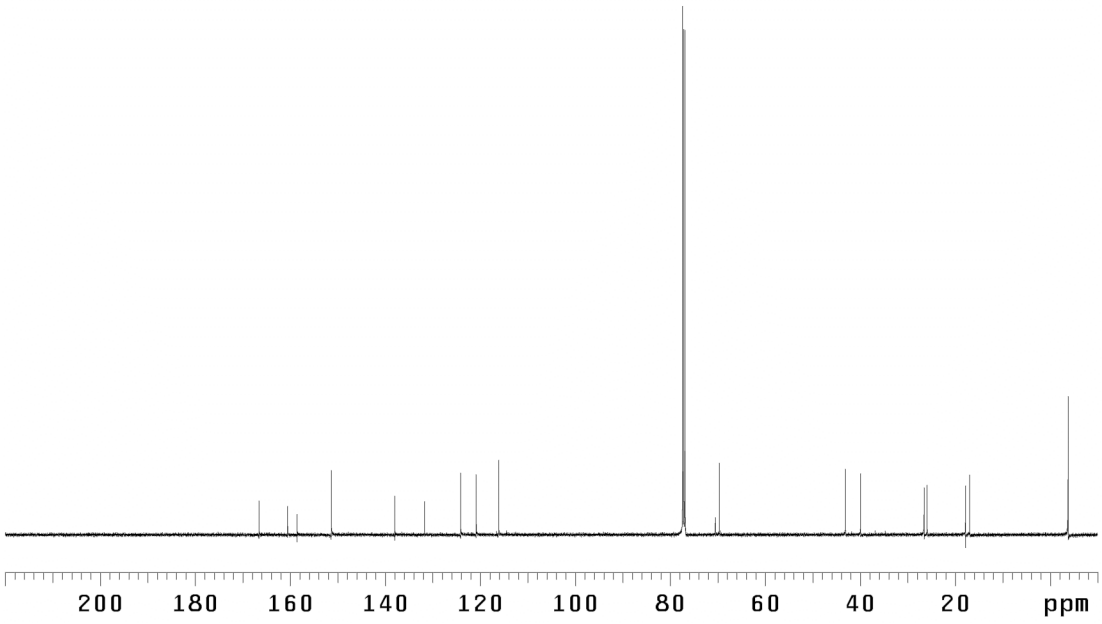


Figure SI-8C ^{13}C NMR (125 MHz, $CDCl_3$) of compound **13**

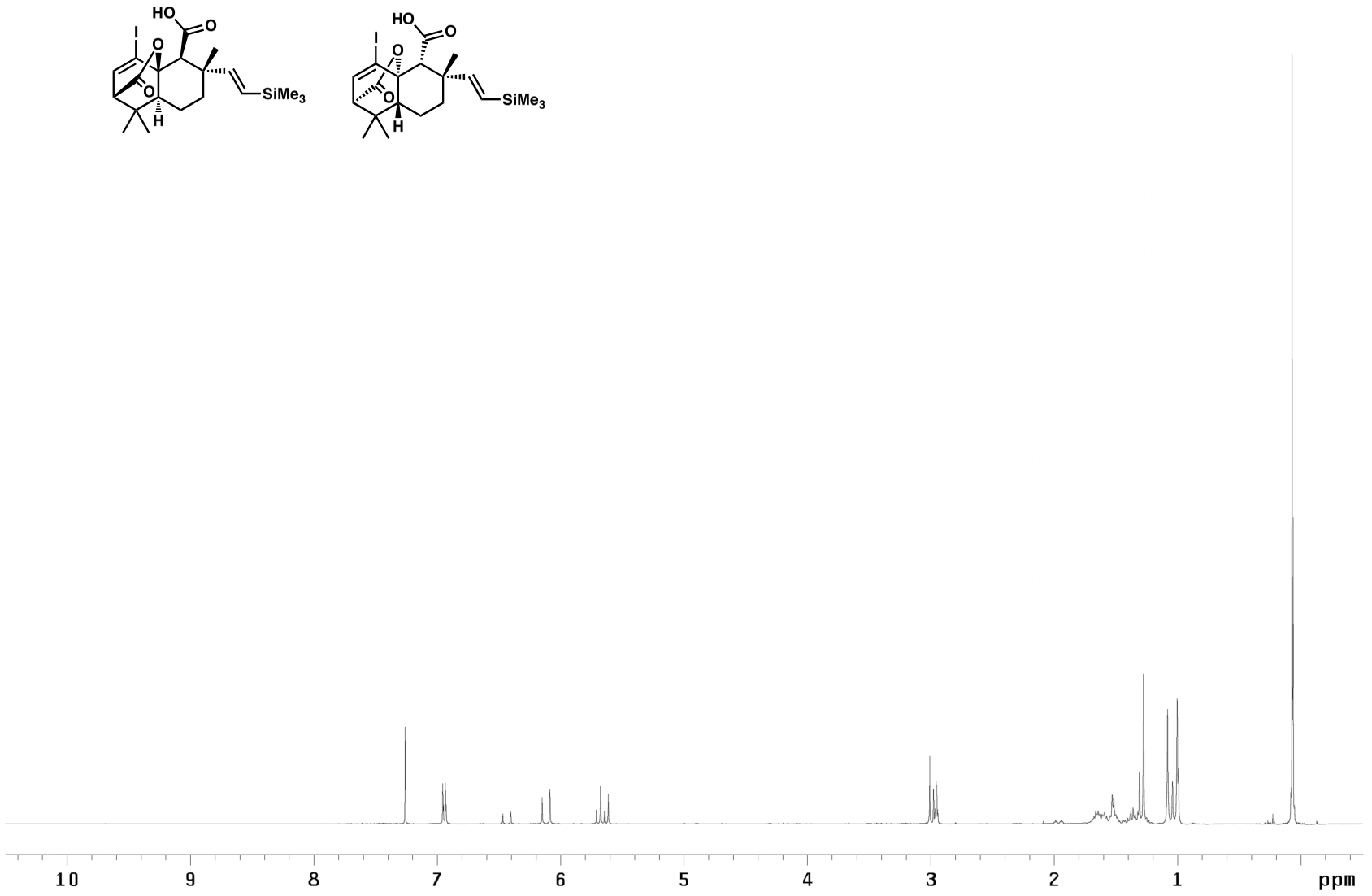


Figure SI-9A ^{1}H NMR (500 MHz, $CDCl_3$) of compounds **18** and **19**

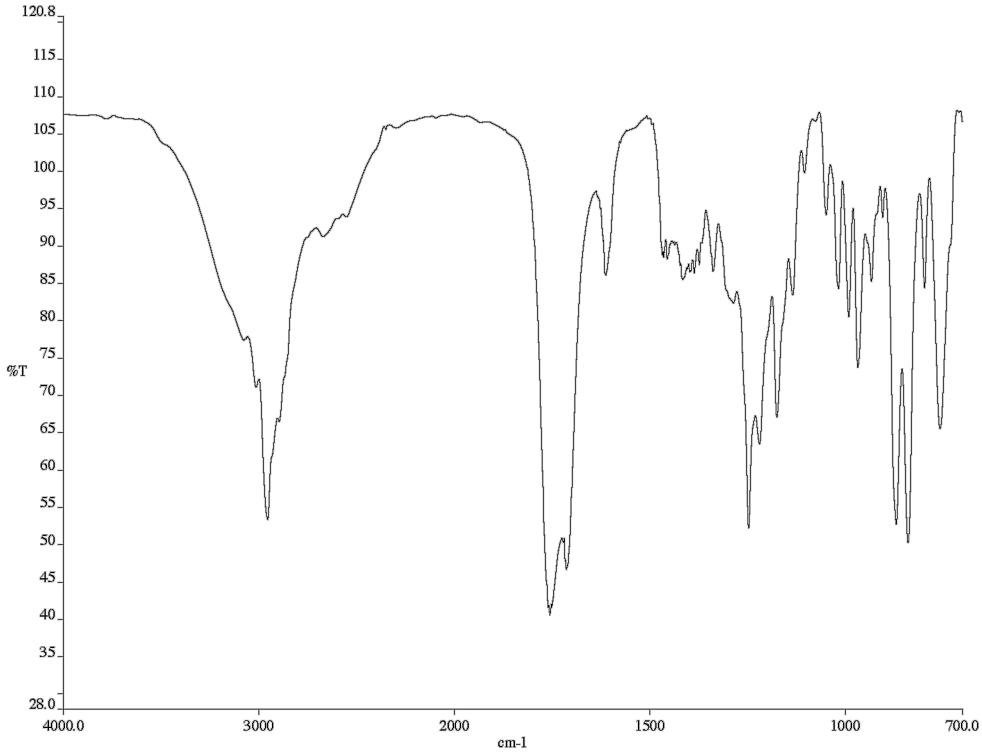


Figure SI-9B Infrared spectrum (thin film/NaCl) of compounds **18** and **19**

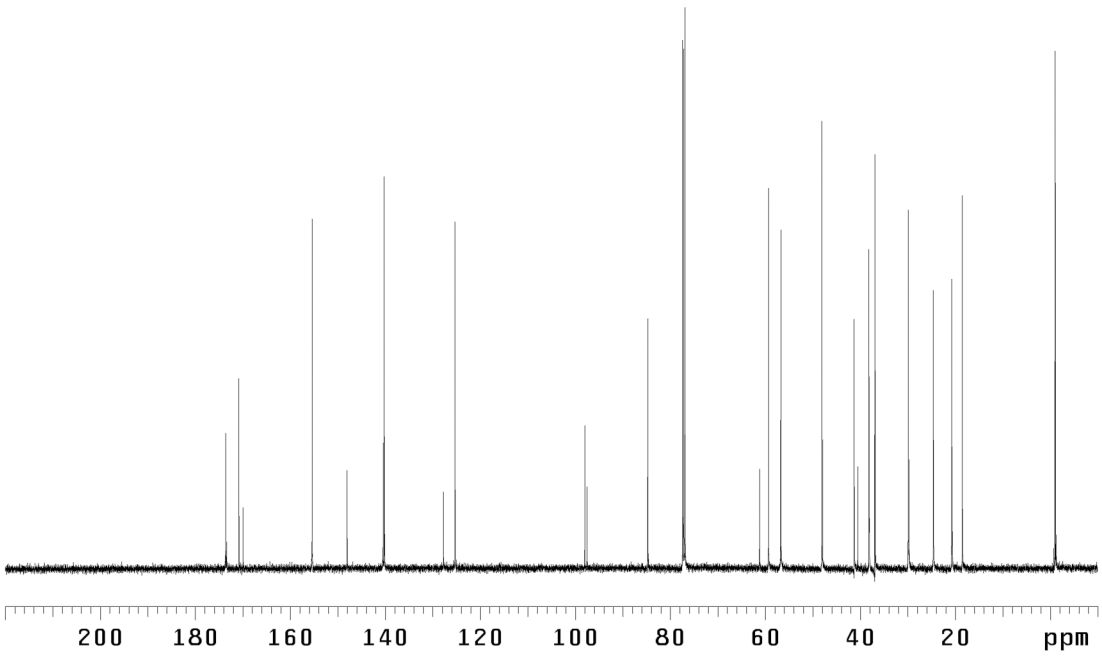


Figure SI-9C ^{13}C NMR (125 MHz, $CDCl_3$) of compounds **18** and **19**

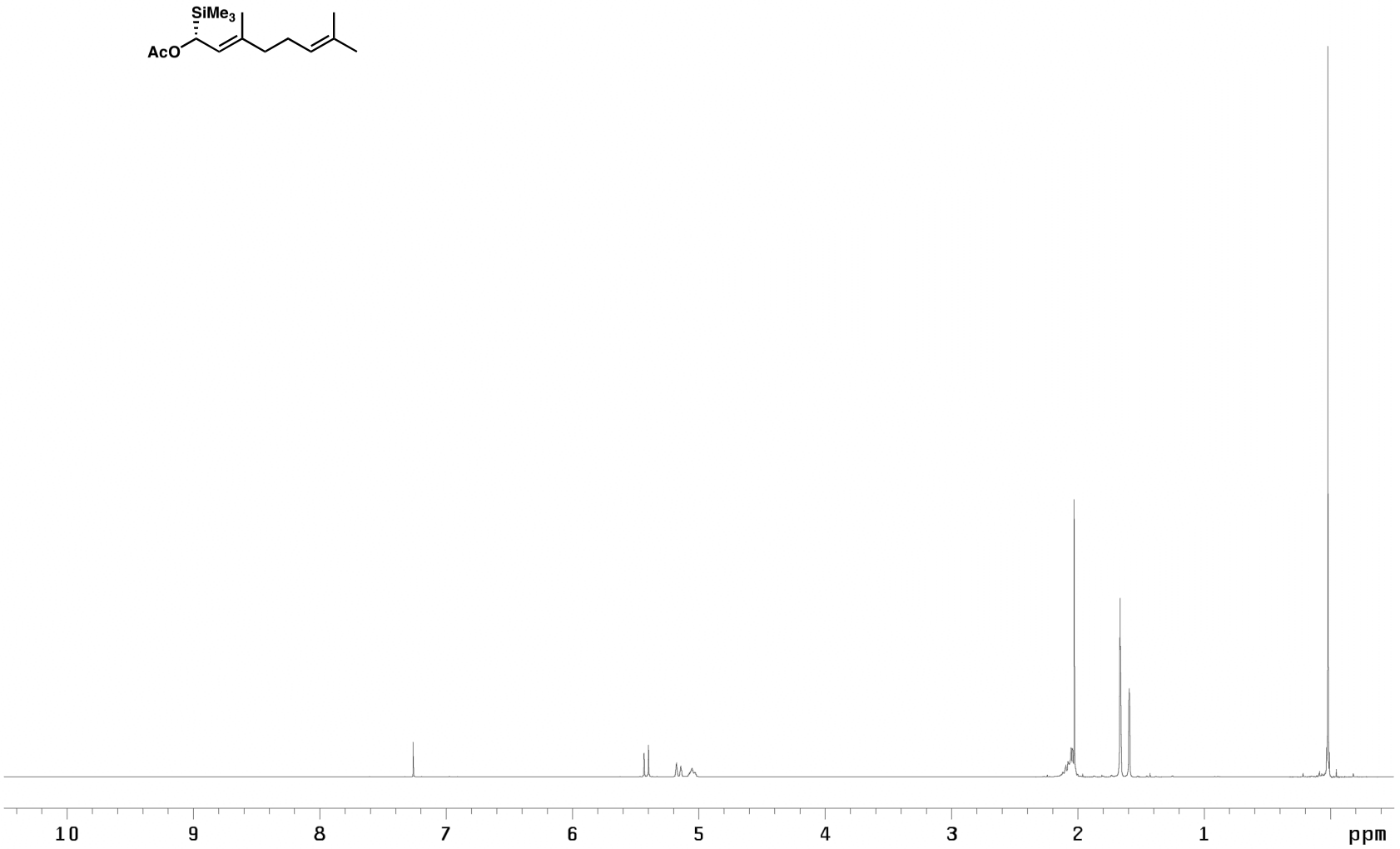


Figure SI-10A ^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI-1**

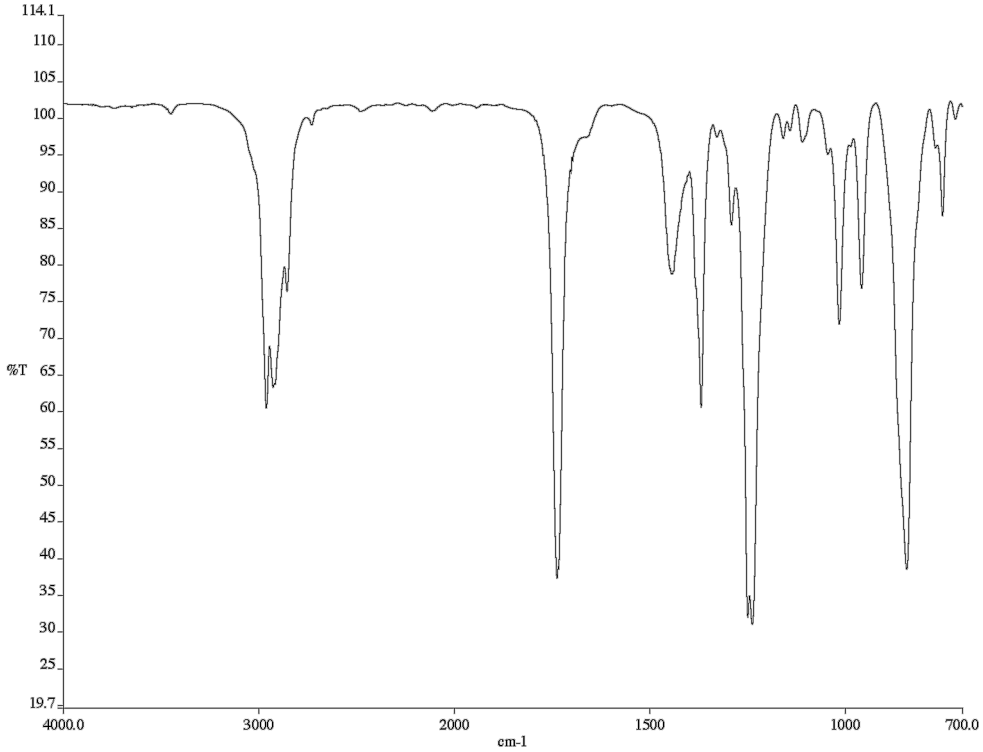


Figure SI-10B Infrared spectrum (thin film/NaCl) of compound **SI-1**

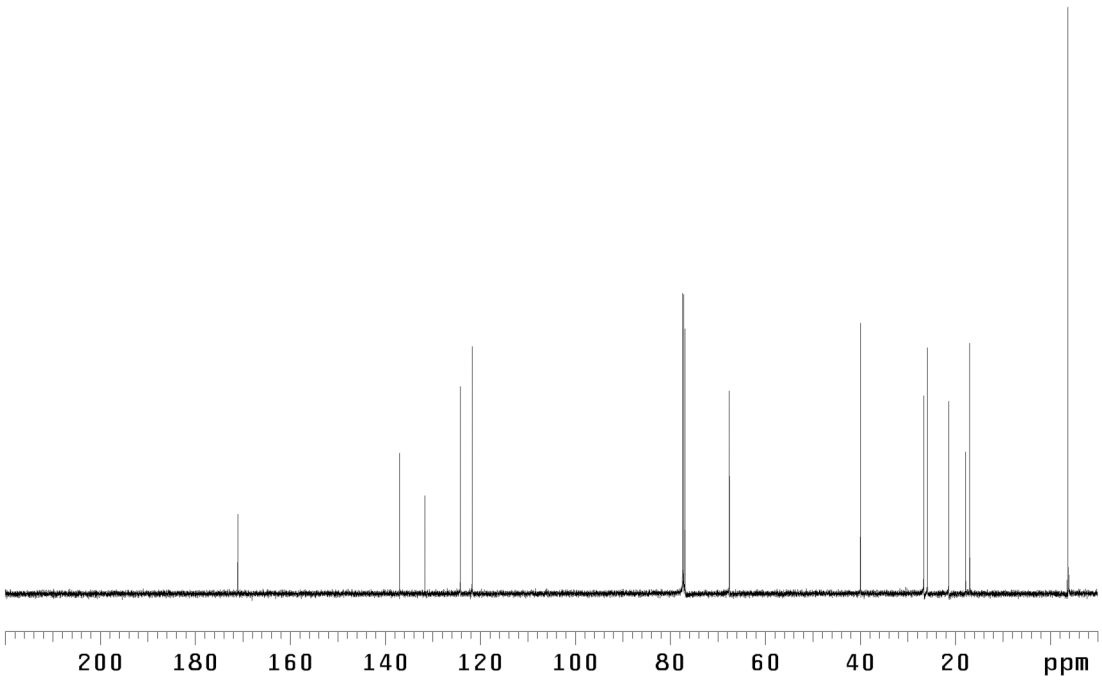


Figure SI-10C ^{13}C NMR (75 MHz, $CDCl_3$) of compound **SI-1**

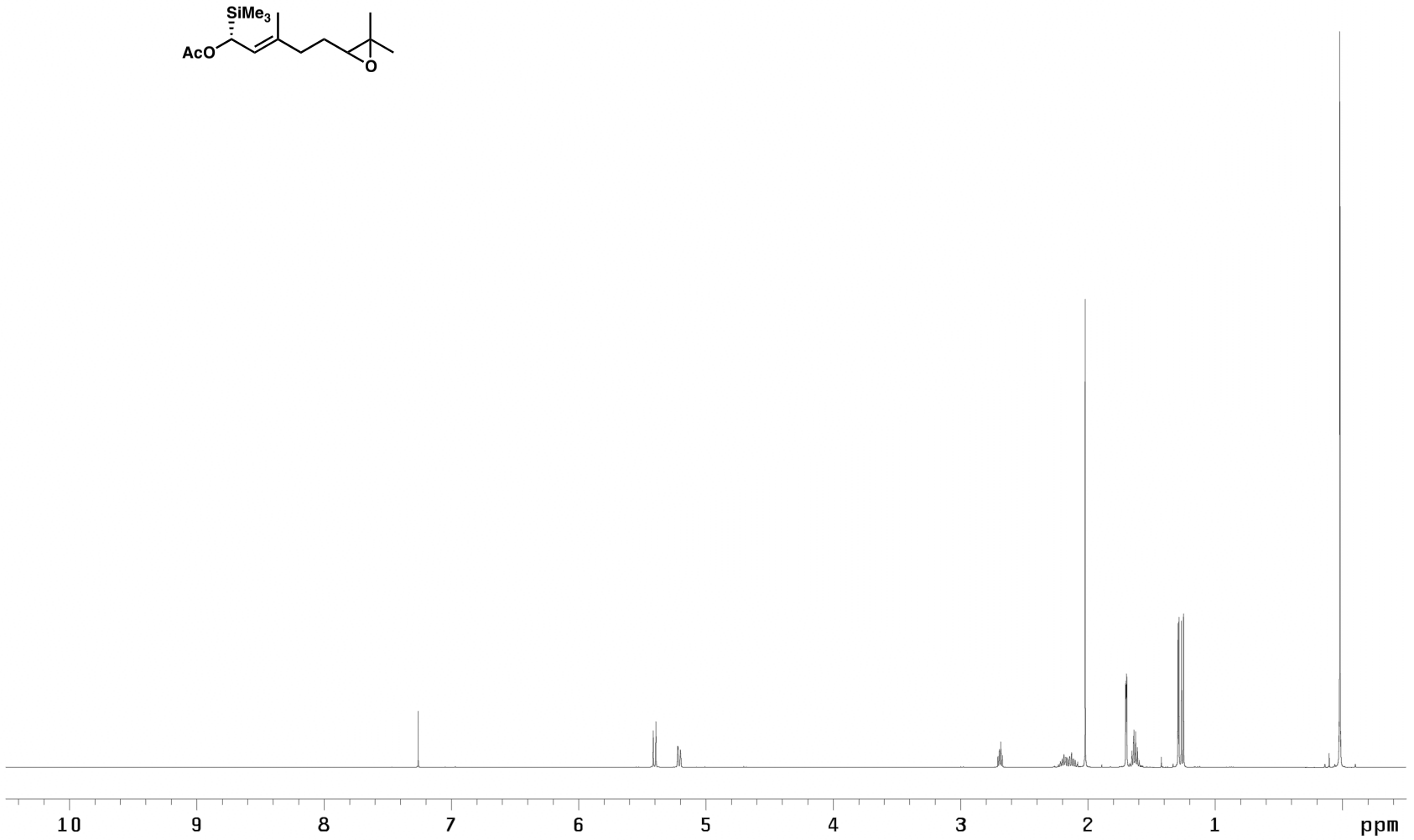


Figure SI-11A ^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-2**

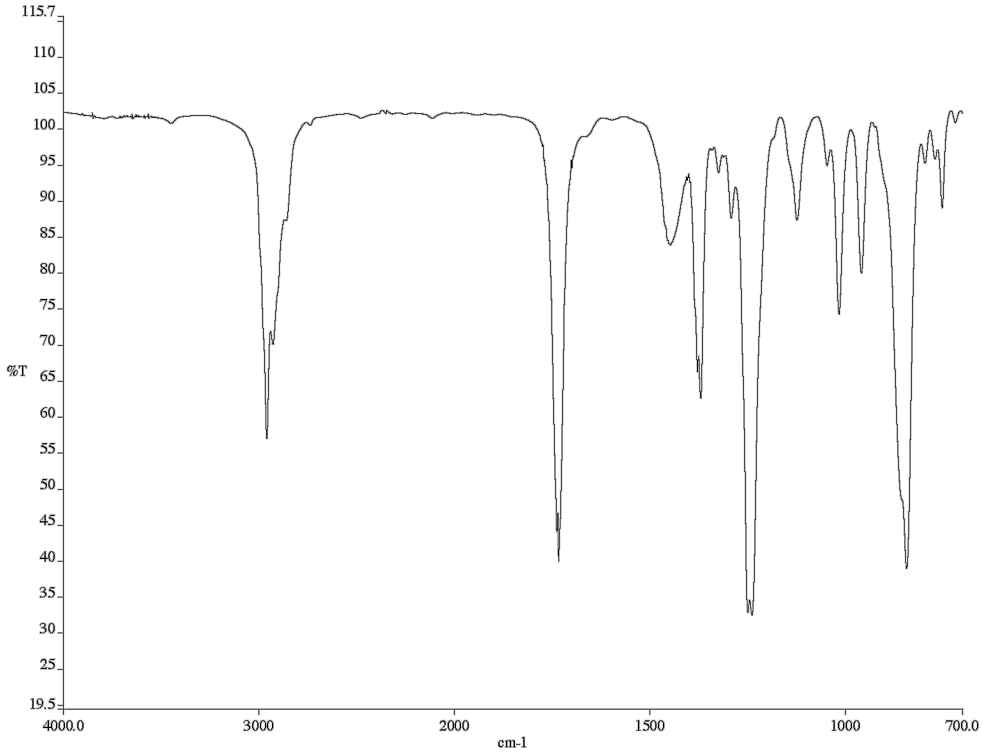


Figure SI-11B Infrared spectrum (thin film/NaCl) of compound **SI-2**

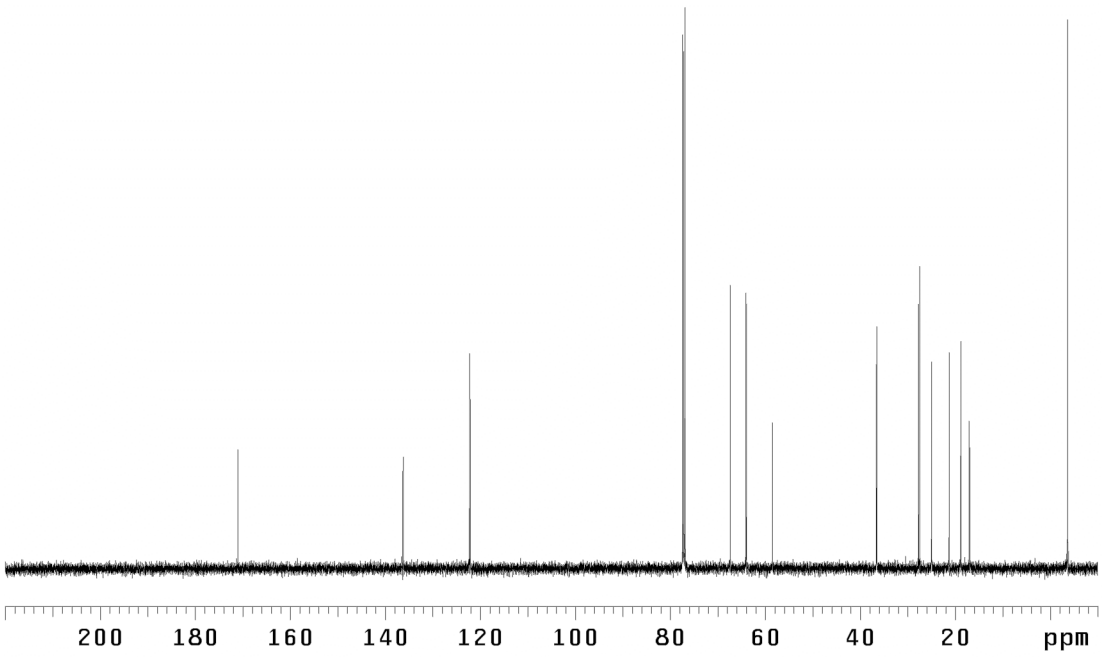


Figure SI-11C ^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-2**

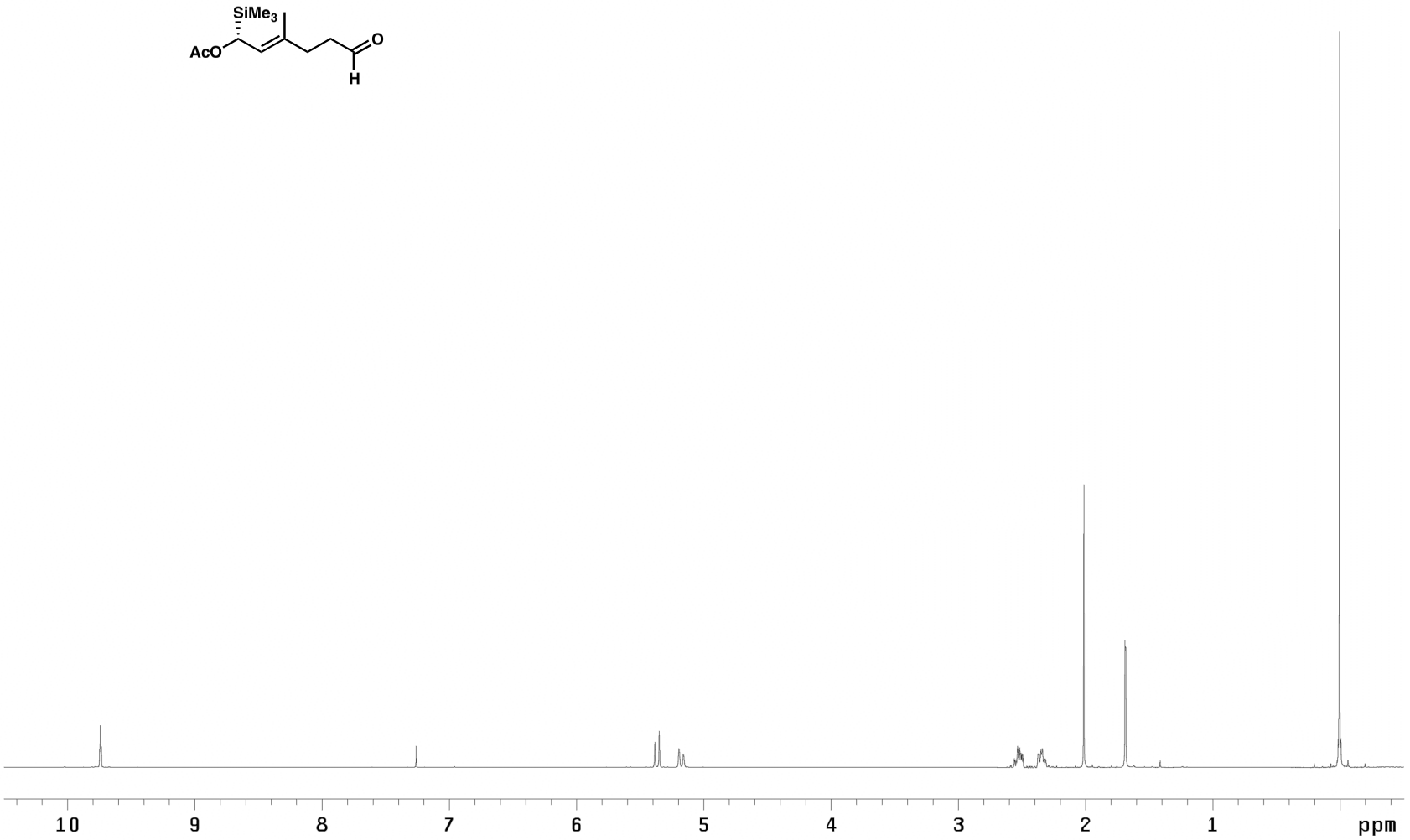


Figure SI-12A ^{1}H NMR (300 MHz, $CDCl_3$) of compound **23**

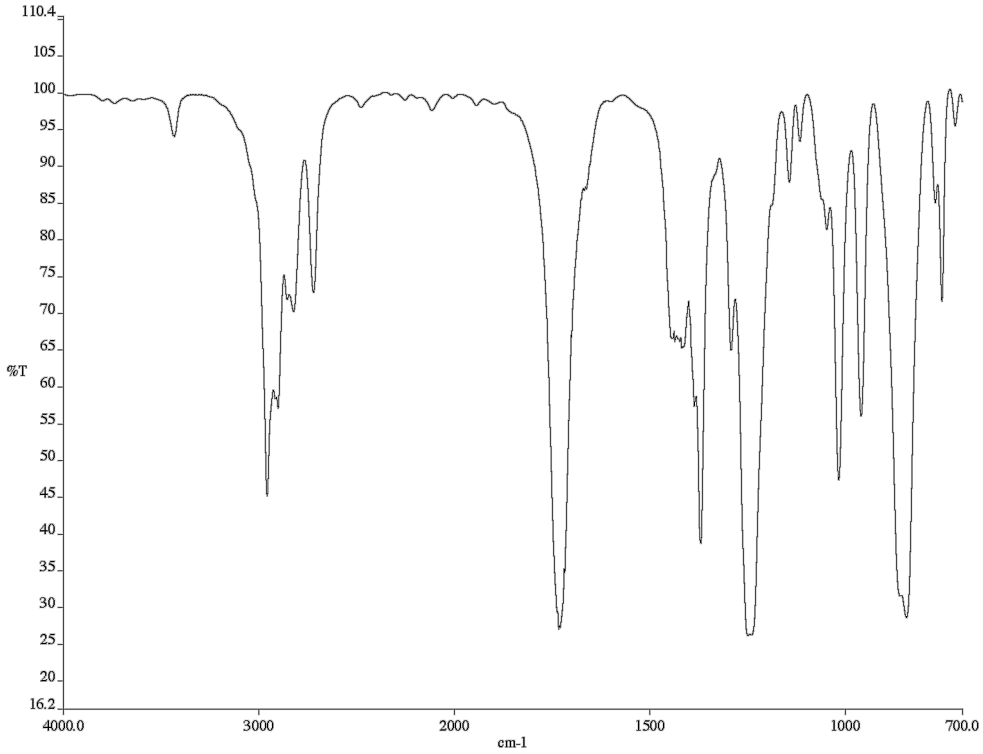


Figure SI-12B Infrared spectrum (thin film/NaCl) of compound **23**

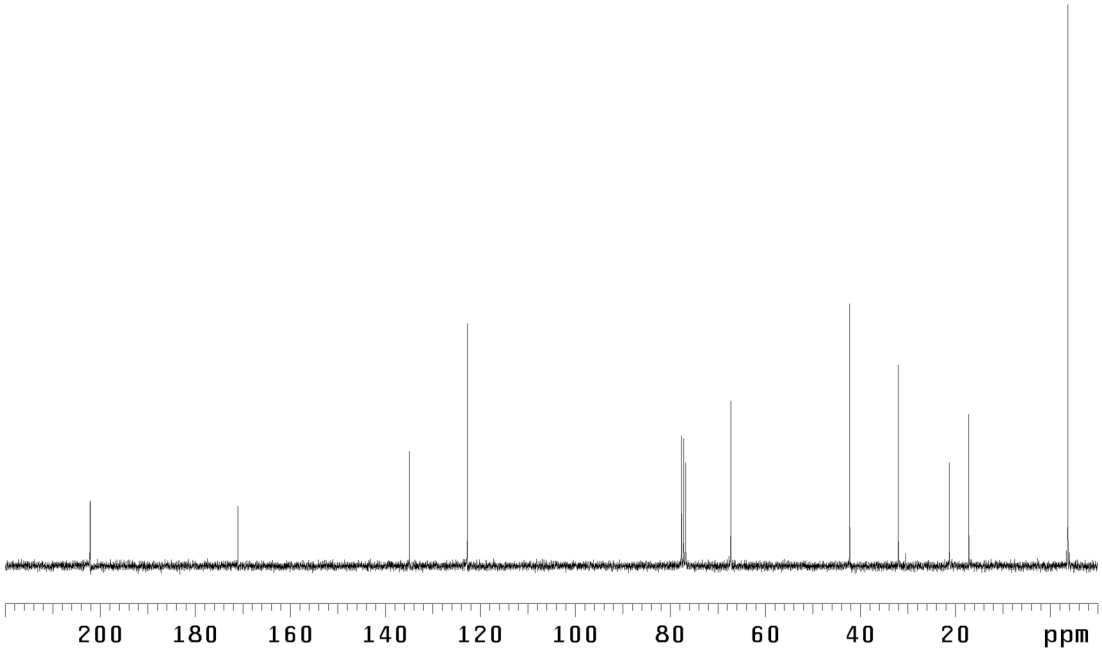


Figure SI-12C ^{13}C NMR (75 MHz, $CDCl_3$) of compound **23**

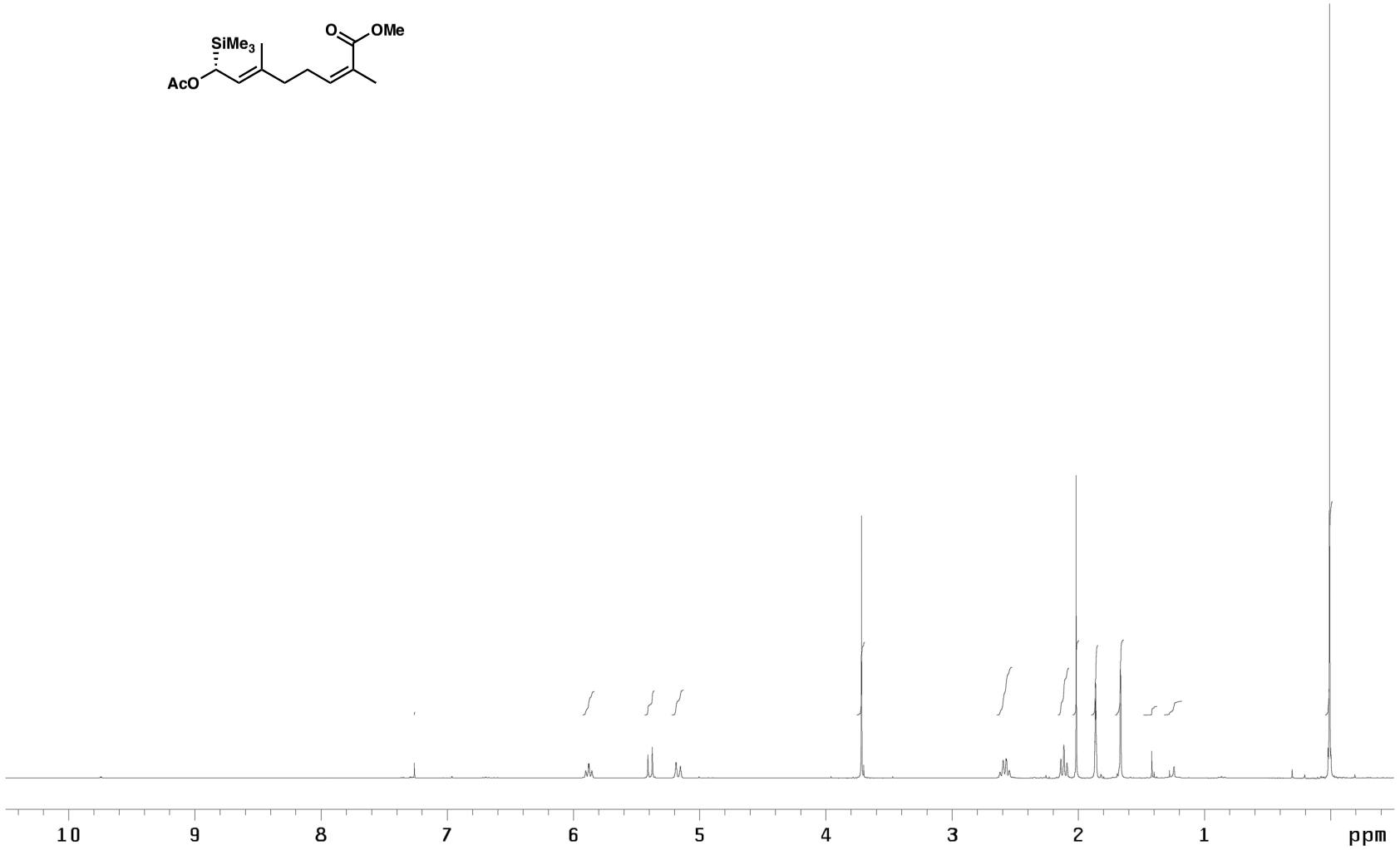


Figure SI-13A ^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI-3**

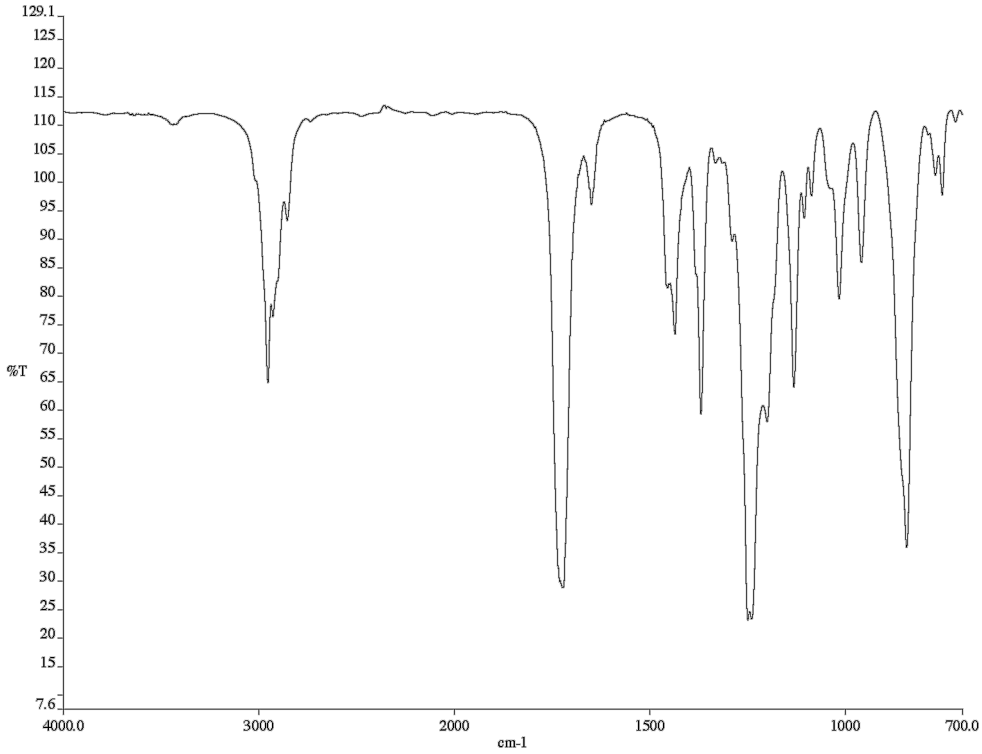


Figure SI-13B Infrared spectrum (thin film/NaCl) of compound **SI-3**

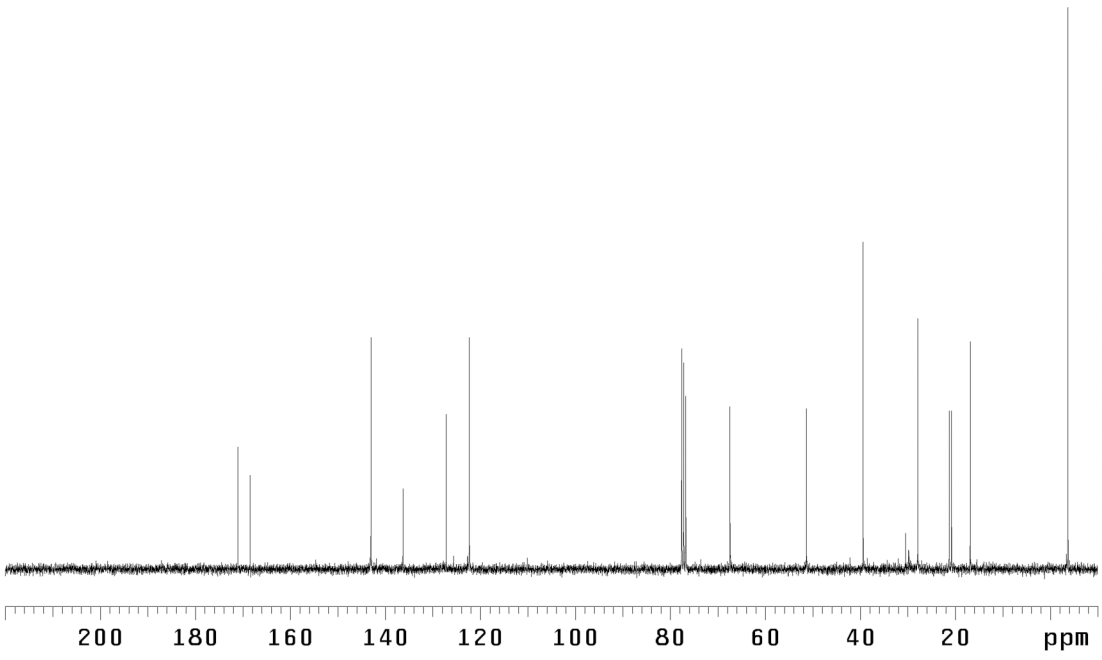


Figure SI-13C ^{13}C NMR (75 MHz, $CDCl_3$) of compound **SI-3**

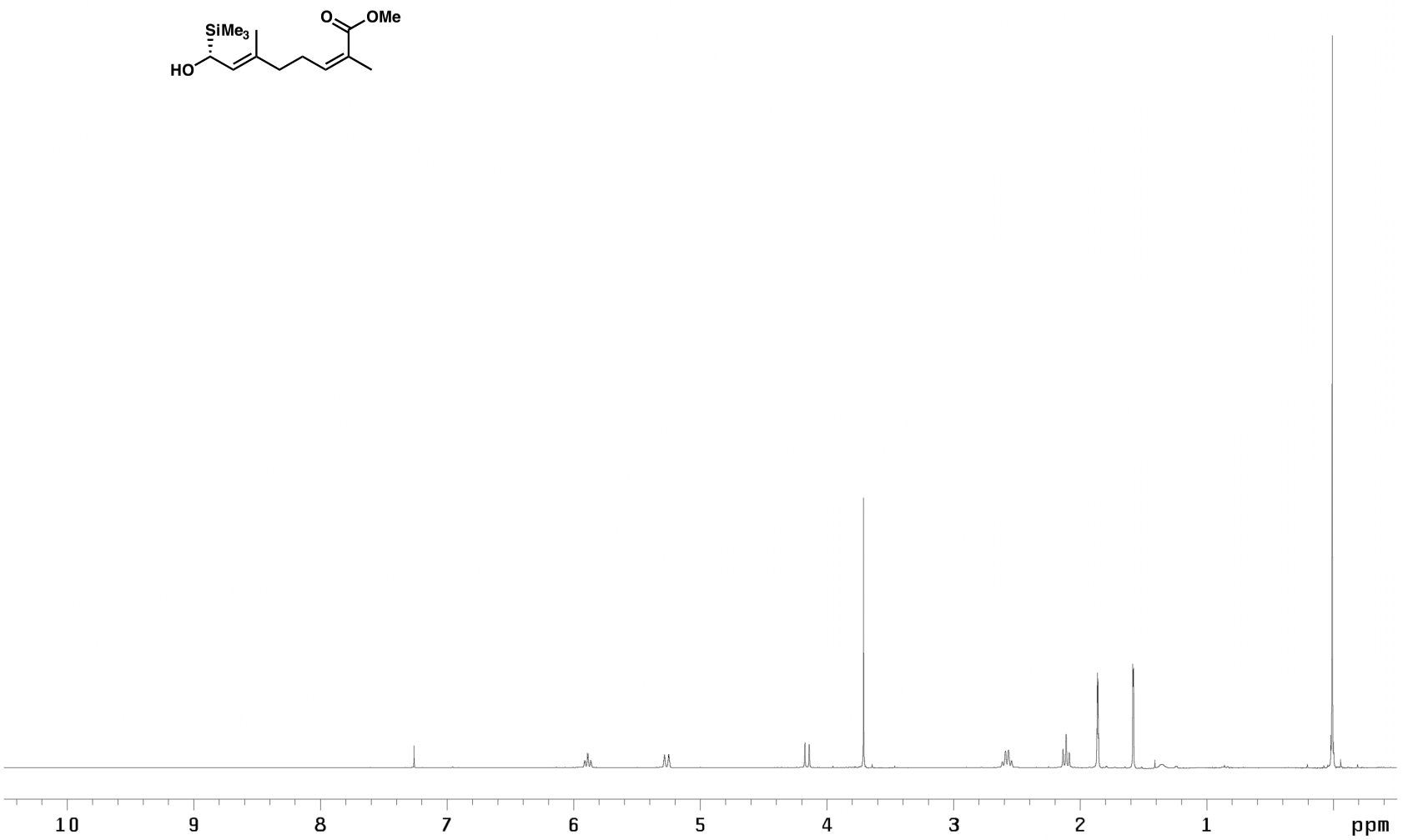


Figure SI-14A ^{1}H NMR (300 MHz, $CDCl_3$) of compound **25**

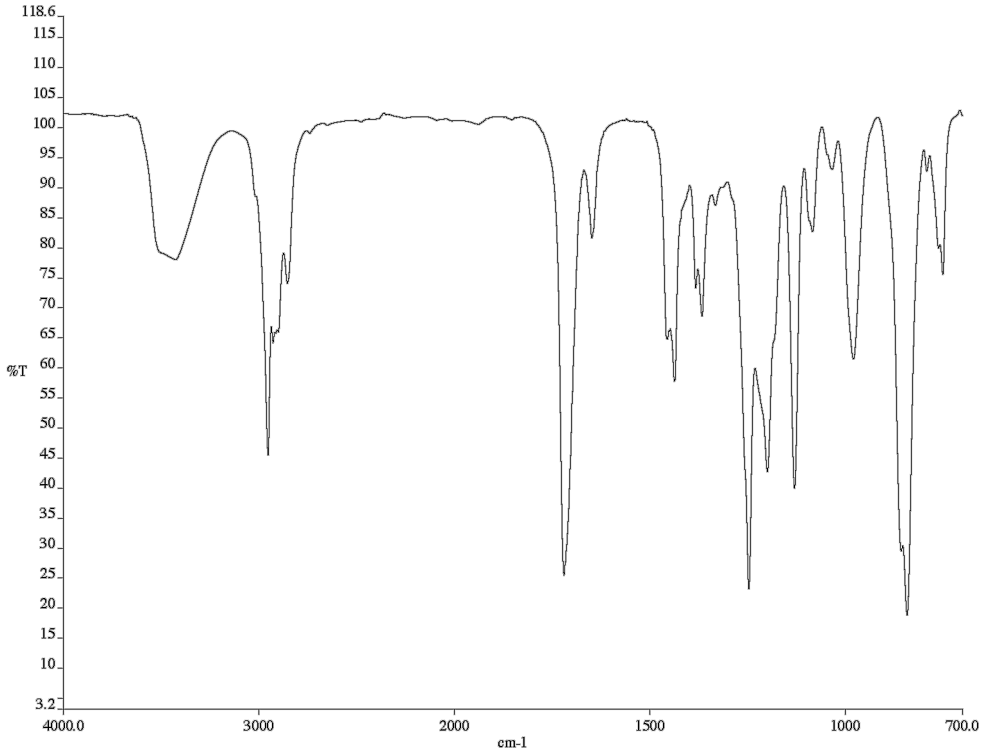


Figure SI-14B Infrared spectrum (thin film/NaCl) of compound **25**

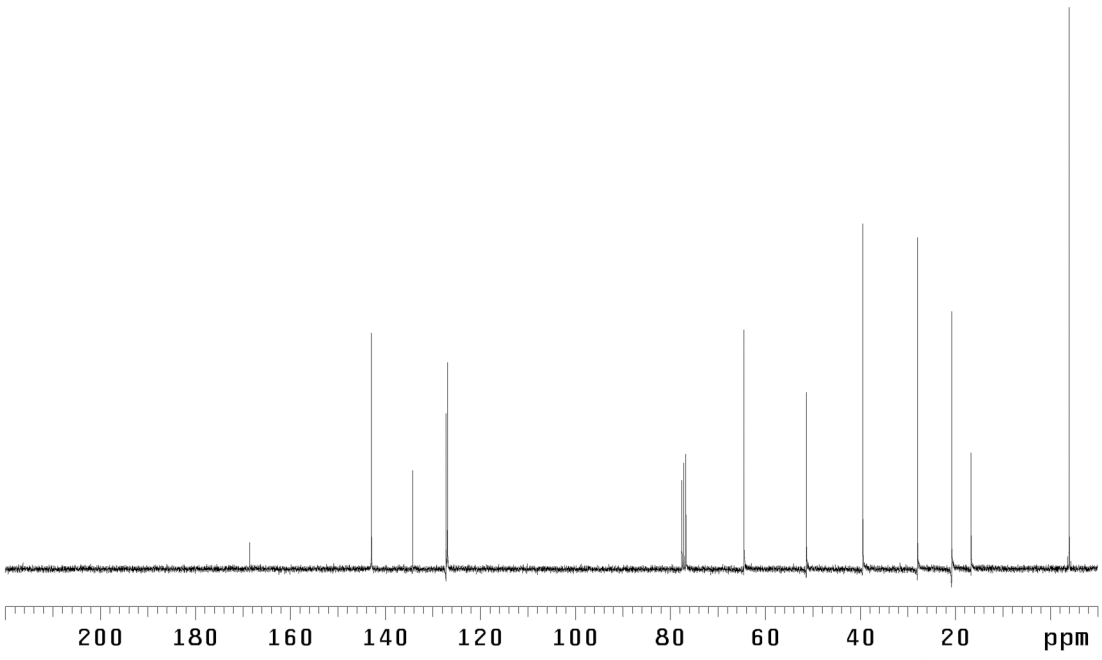


Figure SI-14C ^{13}C NMR (75 MHz, $CDCl_3$) of compound **25**

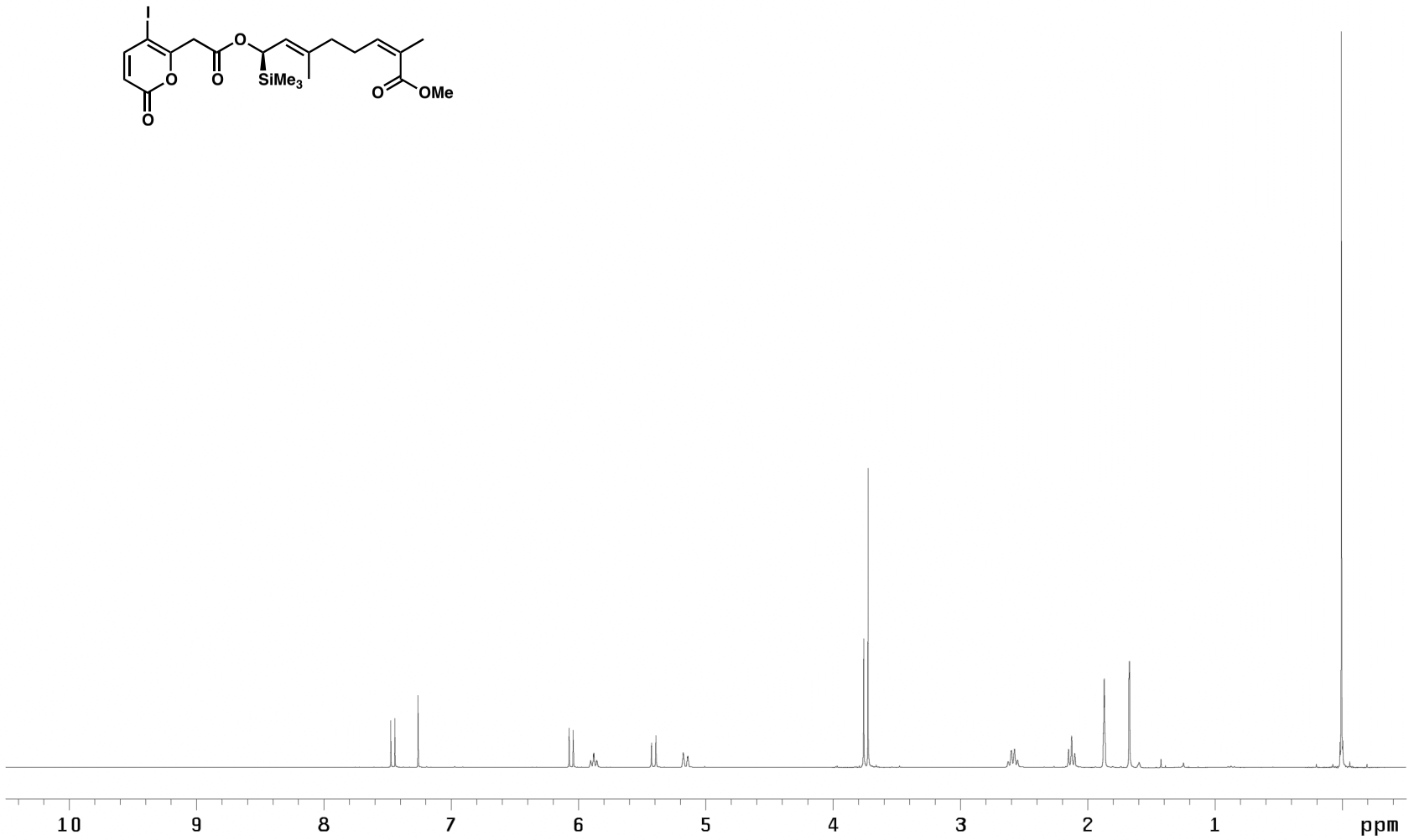


Figure SI-15A ^{1}H NMR (300 MHz, $CDCl_3$) of compound **26**

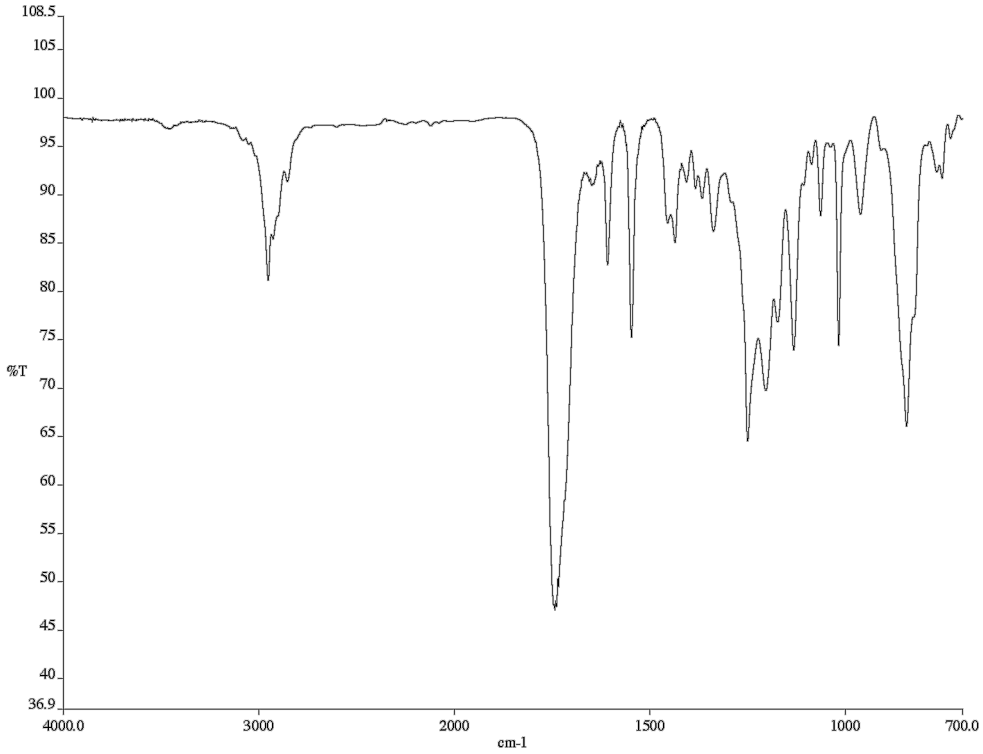


Figure SI-15B Infrared spectrum (thin film/NaCl) of compound **26**

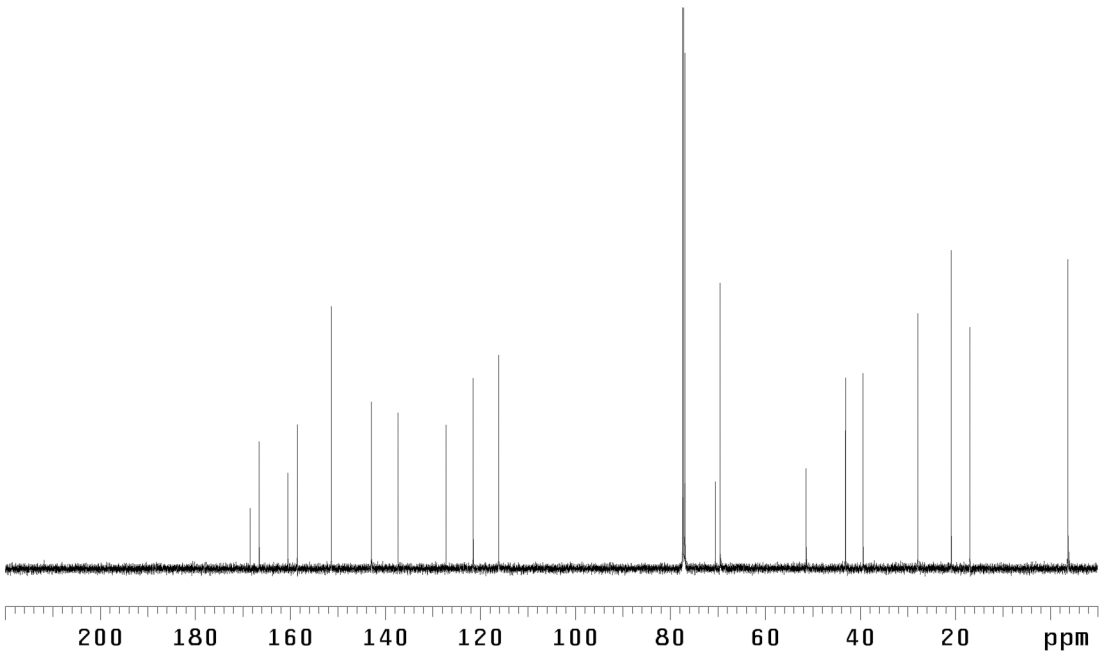
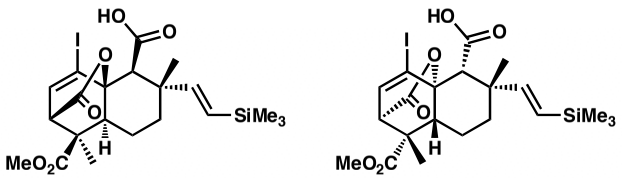


Figure SI-15C ^{13}C NMR (125 MHz, $CDCl_3$) of compound **26**



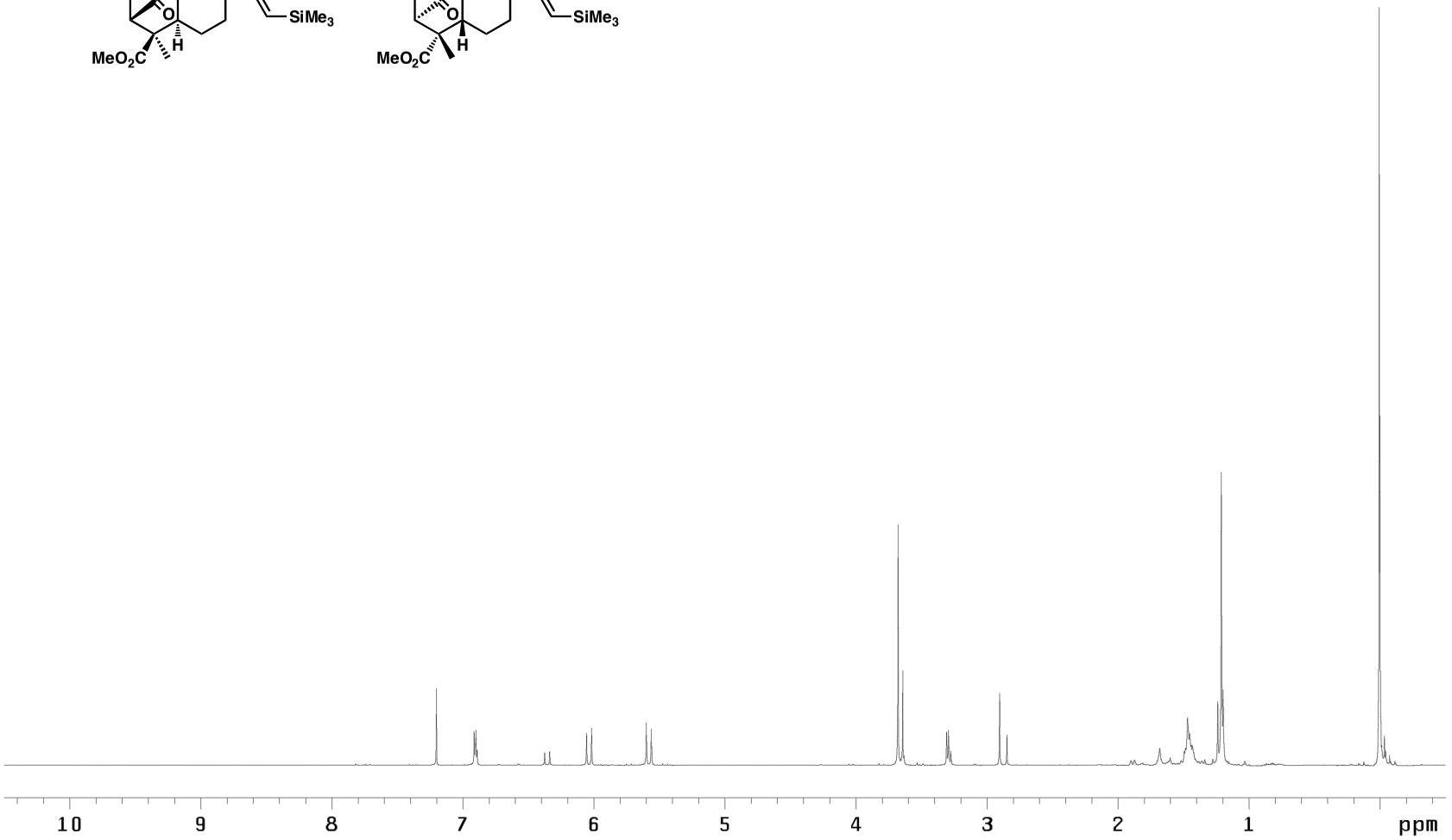


Figure SI-16A ^{1}H NMR (500 MHz, $CDCl_3$) of compounds **27** and **28**

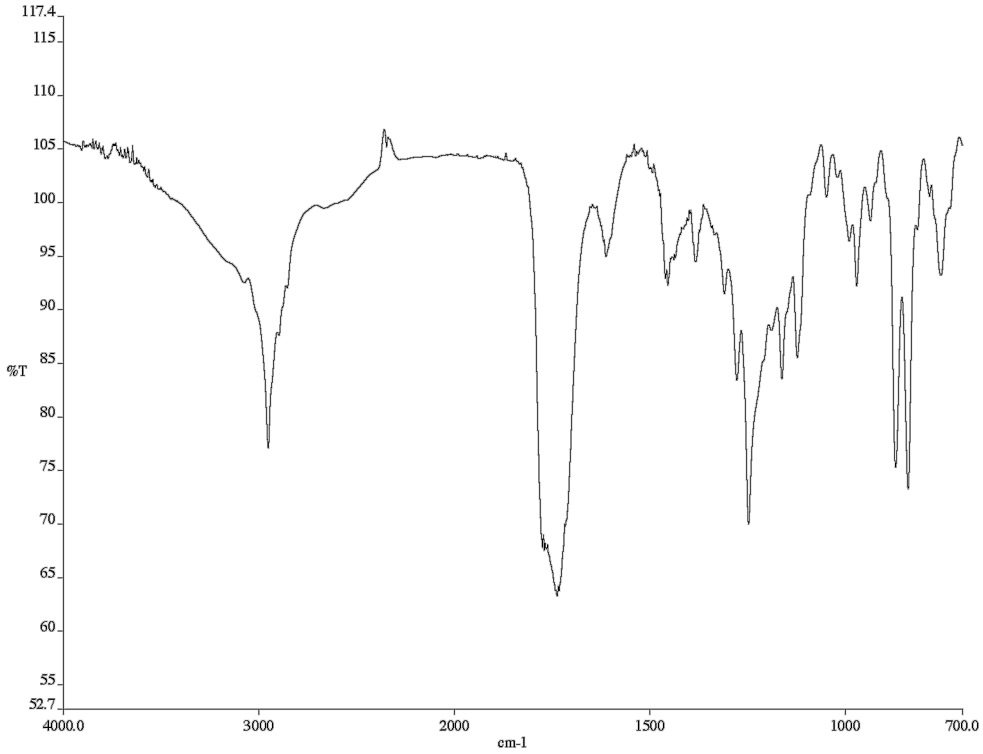


Figure SI-16B Infrared spectrum (thin film/NaCl) of compounds **27** and **28**

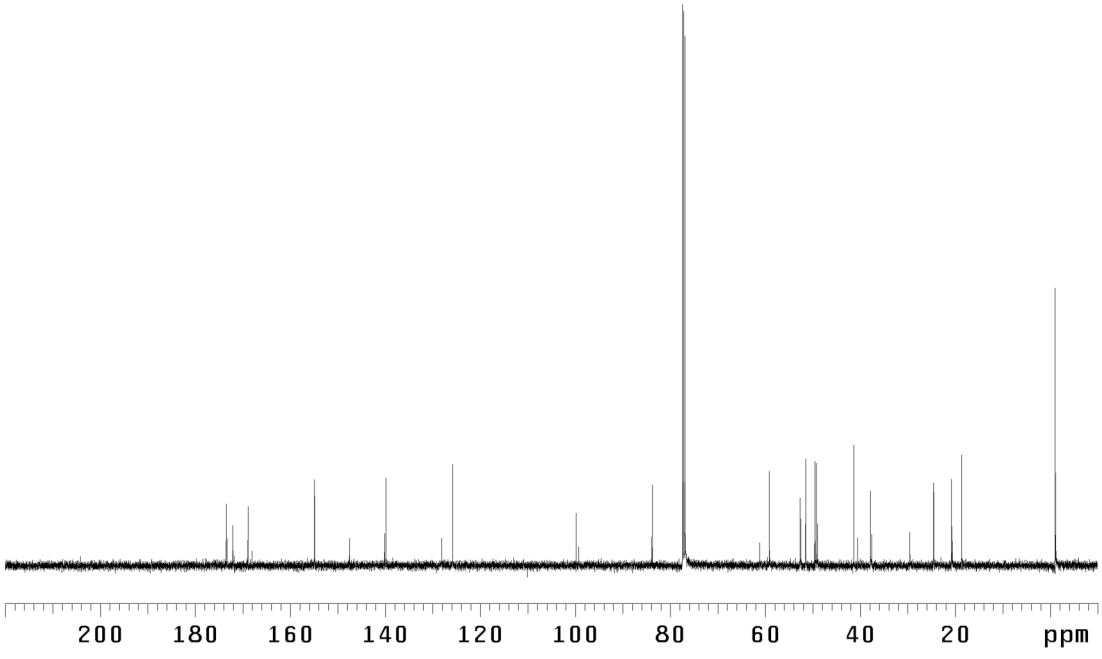


Figure SI-16C ^{13}C NMR (125 MHz, $CDCl_3$) of compounds **27** and **28**

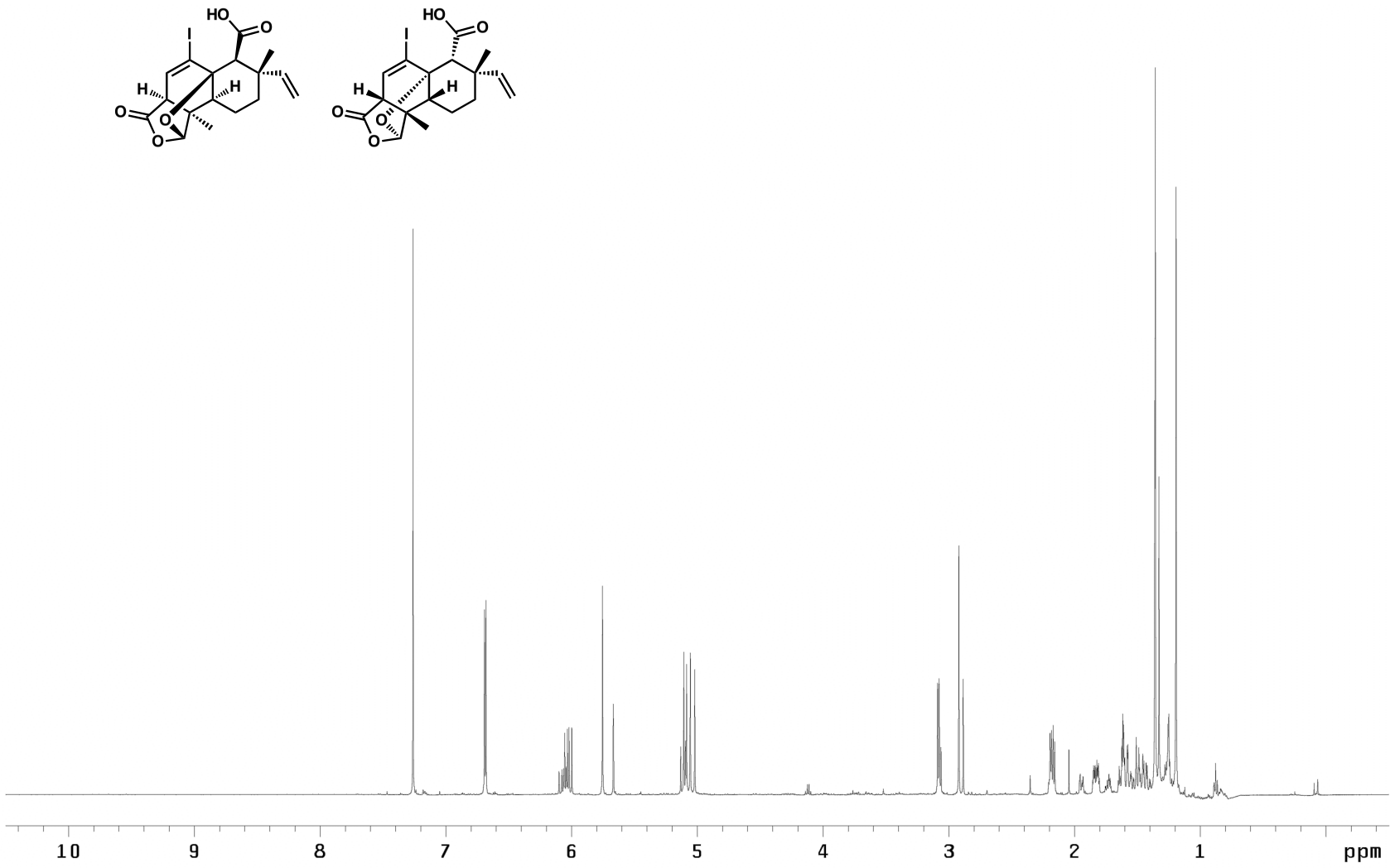


Figure SI-17A ^{1}H NMR (500 MHz, $CDCl_3$) of compounds **10a** and **10b**

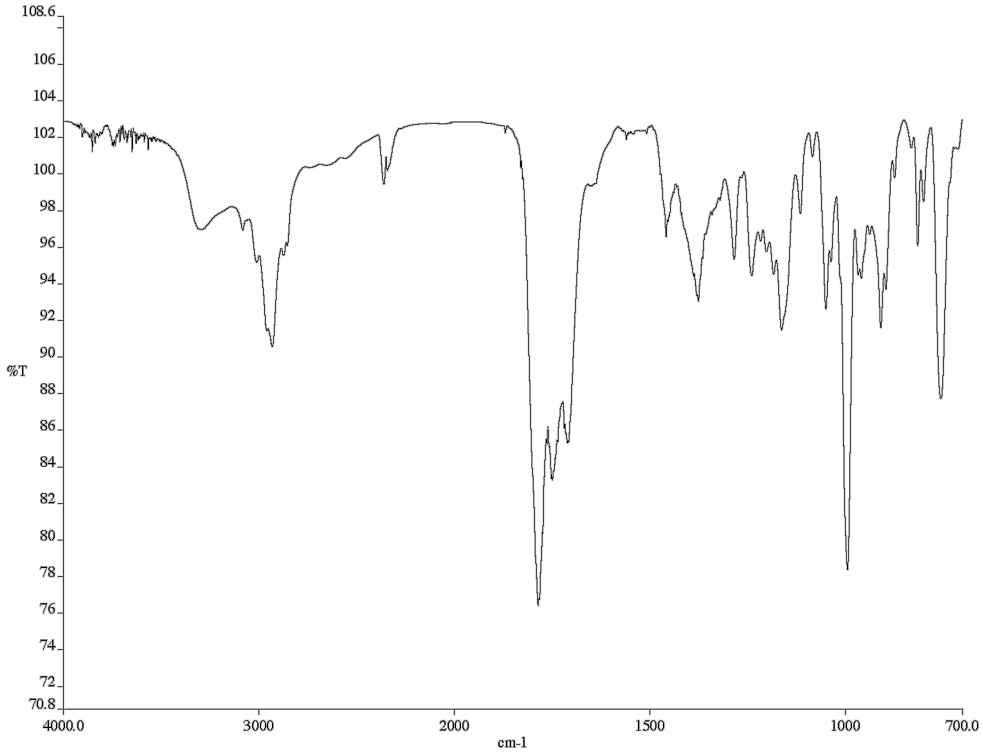


Figure SI-17B Infrared spectrum (thin film/NaCl) of compounds **10a** and **10b**

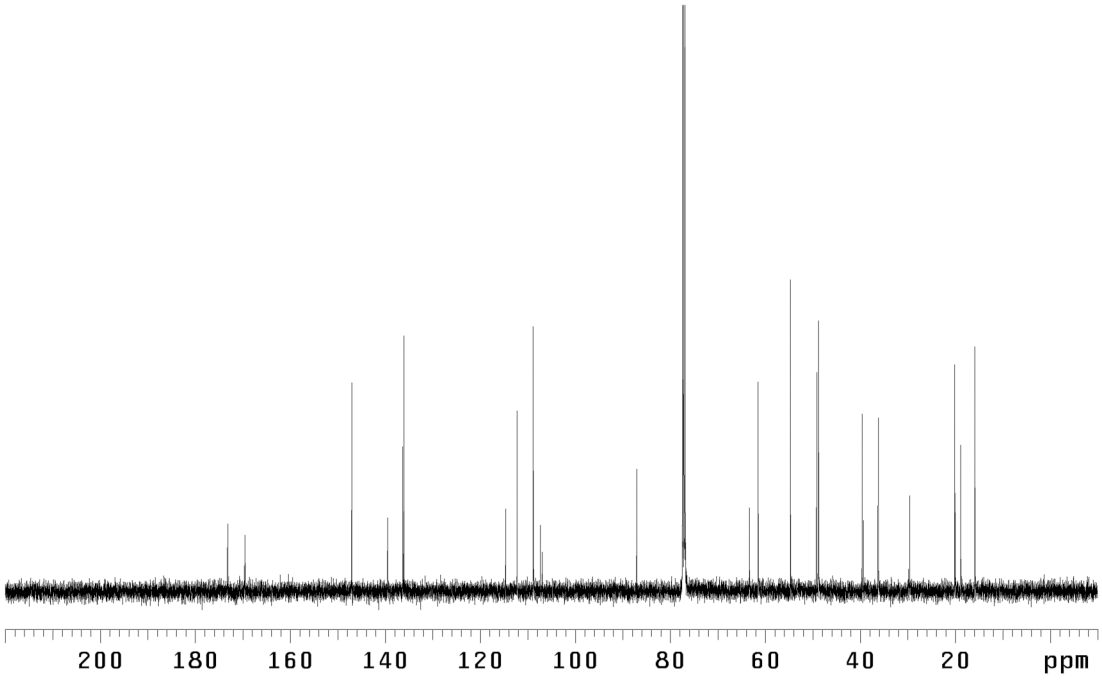


Figure SI-17C ^{13}C NMR (125 MHz, $CDCl_3$) of compounds **10a** and **10b**

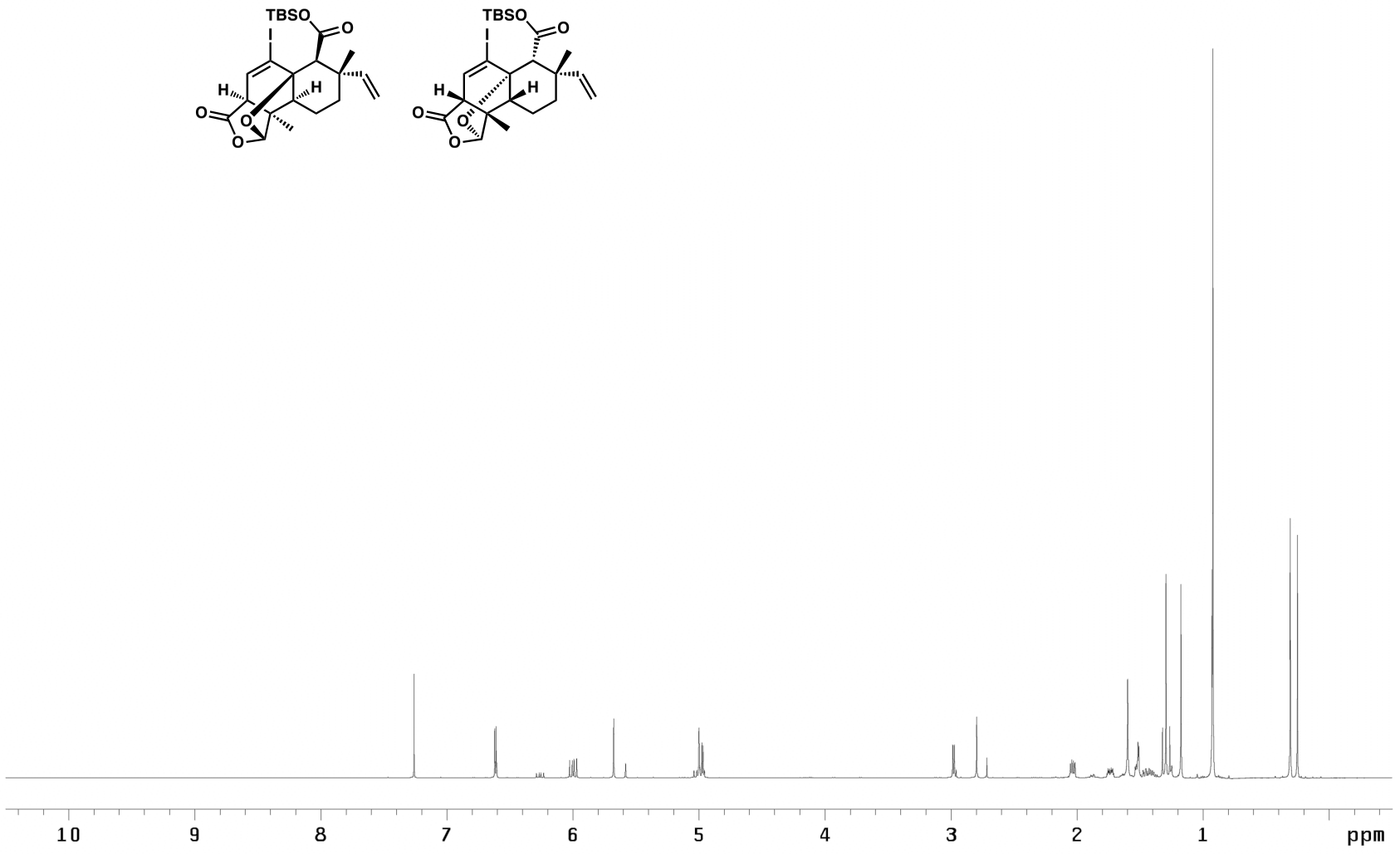


Figure SI-18A ^{1}H NMR (500 MHz, $CDCl_3$) of compounds **10c** and **10d**

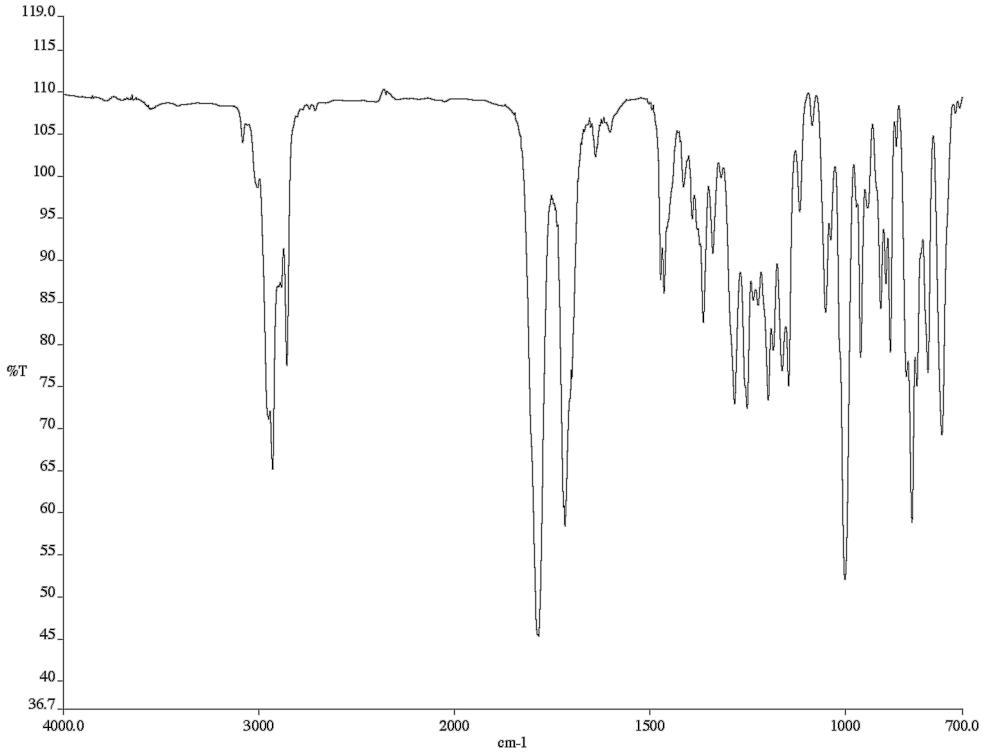


Figure SI-18B Infrared spectrum (thin film/NaCl) of compounds **10c** and **10d**

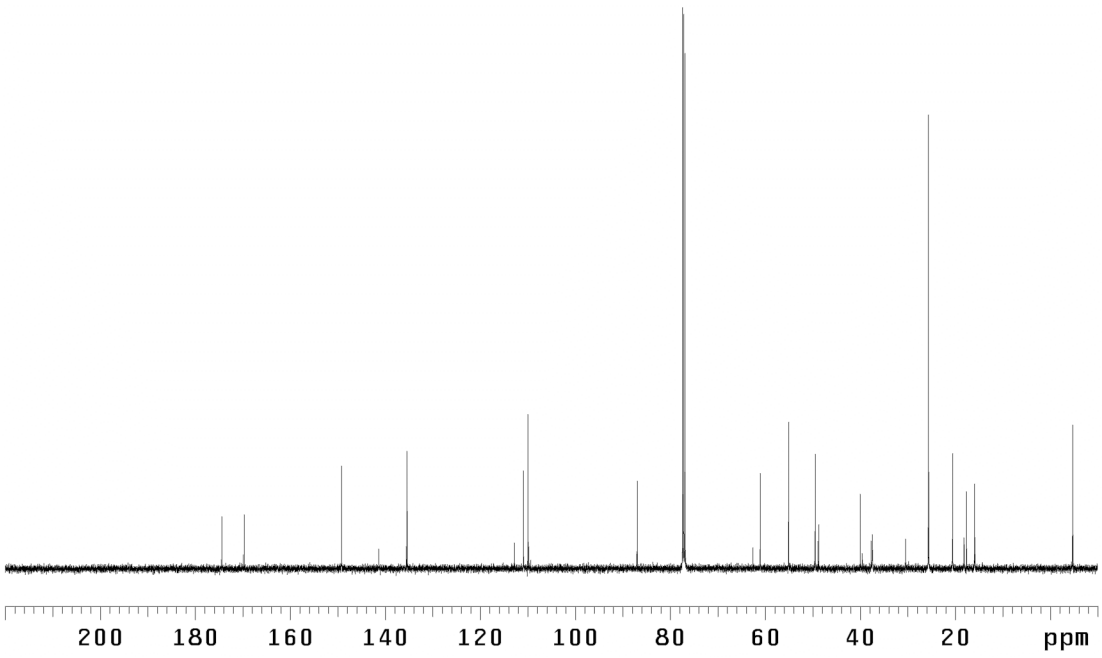


Figure SI-18C ^{13}C NMR (125 MHz, $CDCl_3$) of compounds **10c** and **10b**

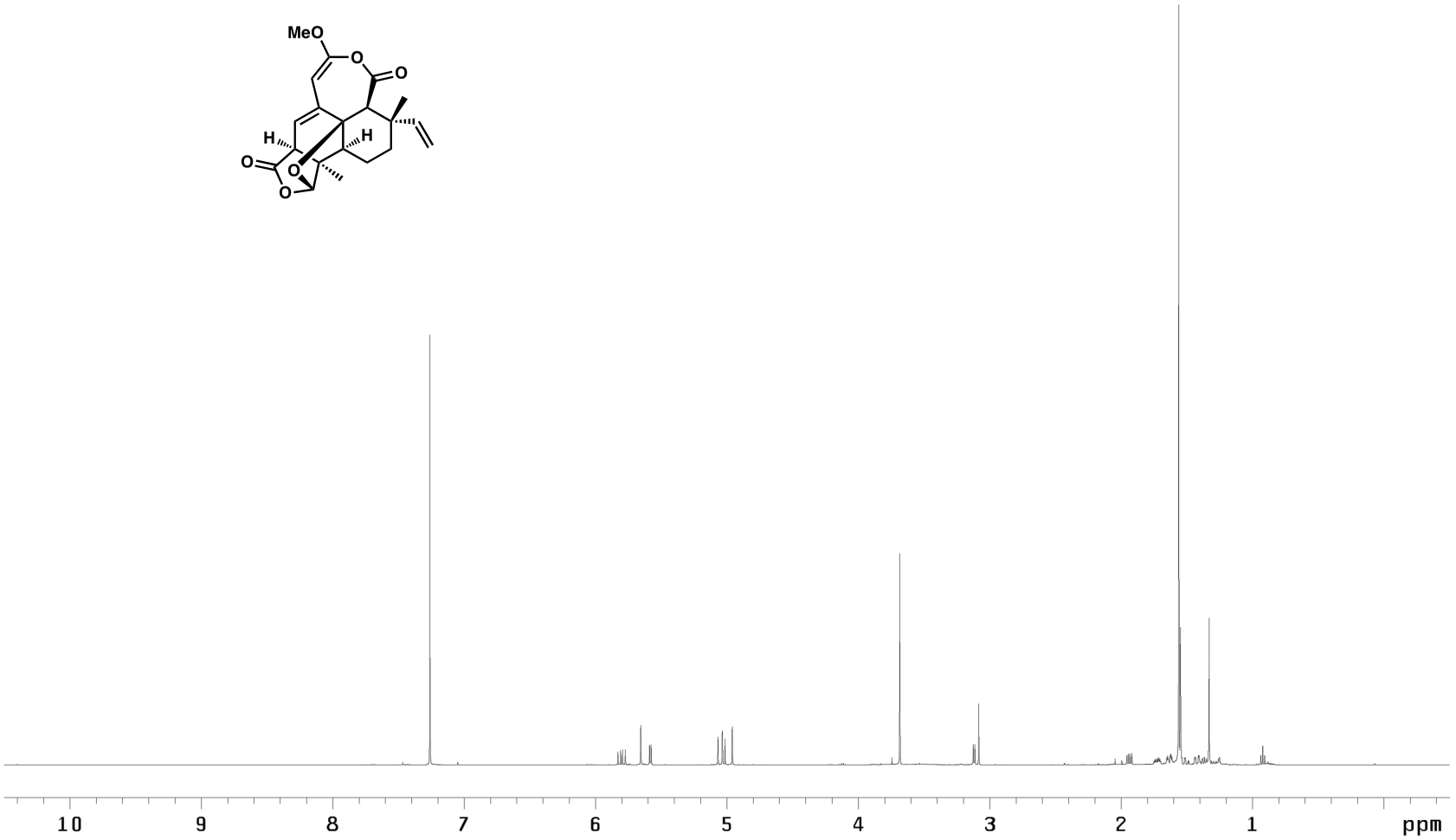


Figure SI-19A ^{1}H NMR (500 MHz, $CDCl_3$) of transtaganolide B (**2**)

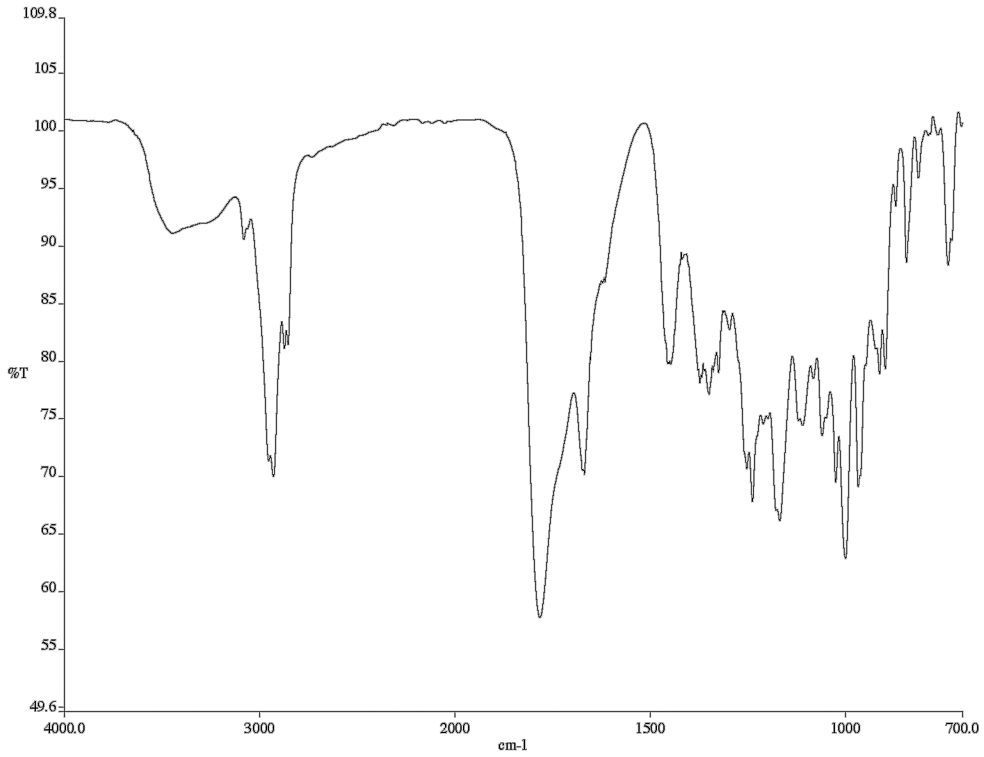


Figure SI-19B Infrared spectrum (thin film/NaCl) of transtaganolide B (**2**)

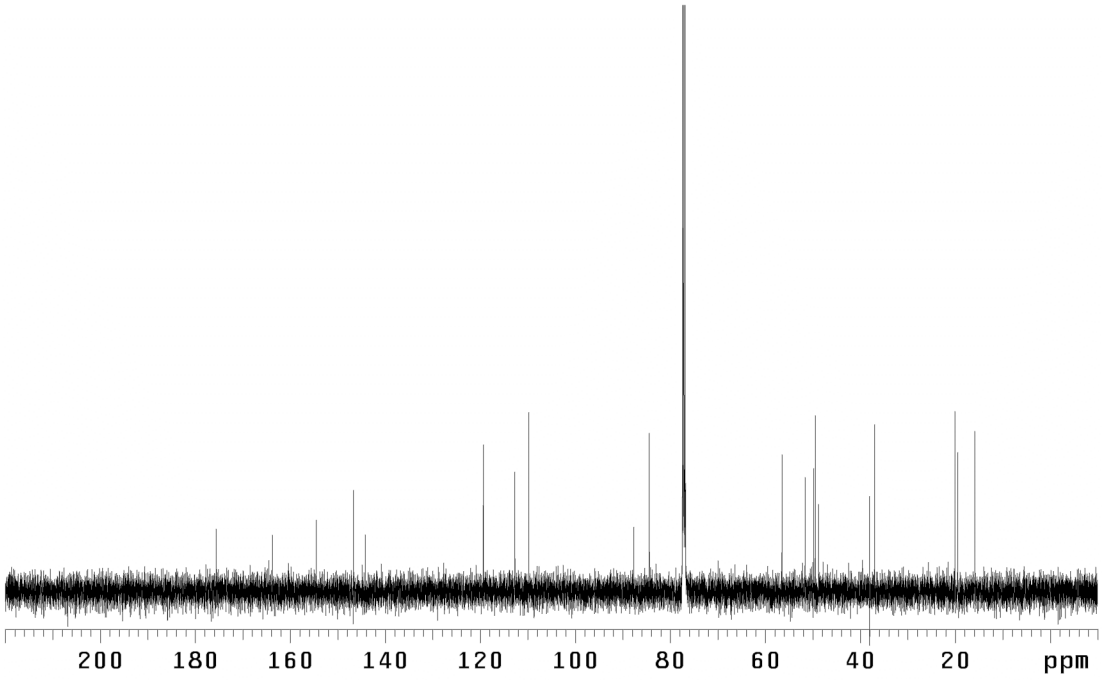


Figure SI-19C ^{13}C NMR (125 MHz, $CDCl_3$) of transtaganolide B (**2**)

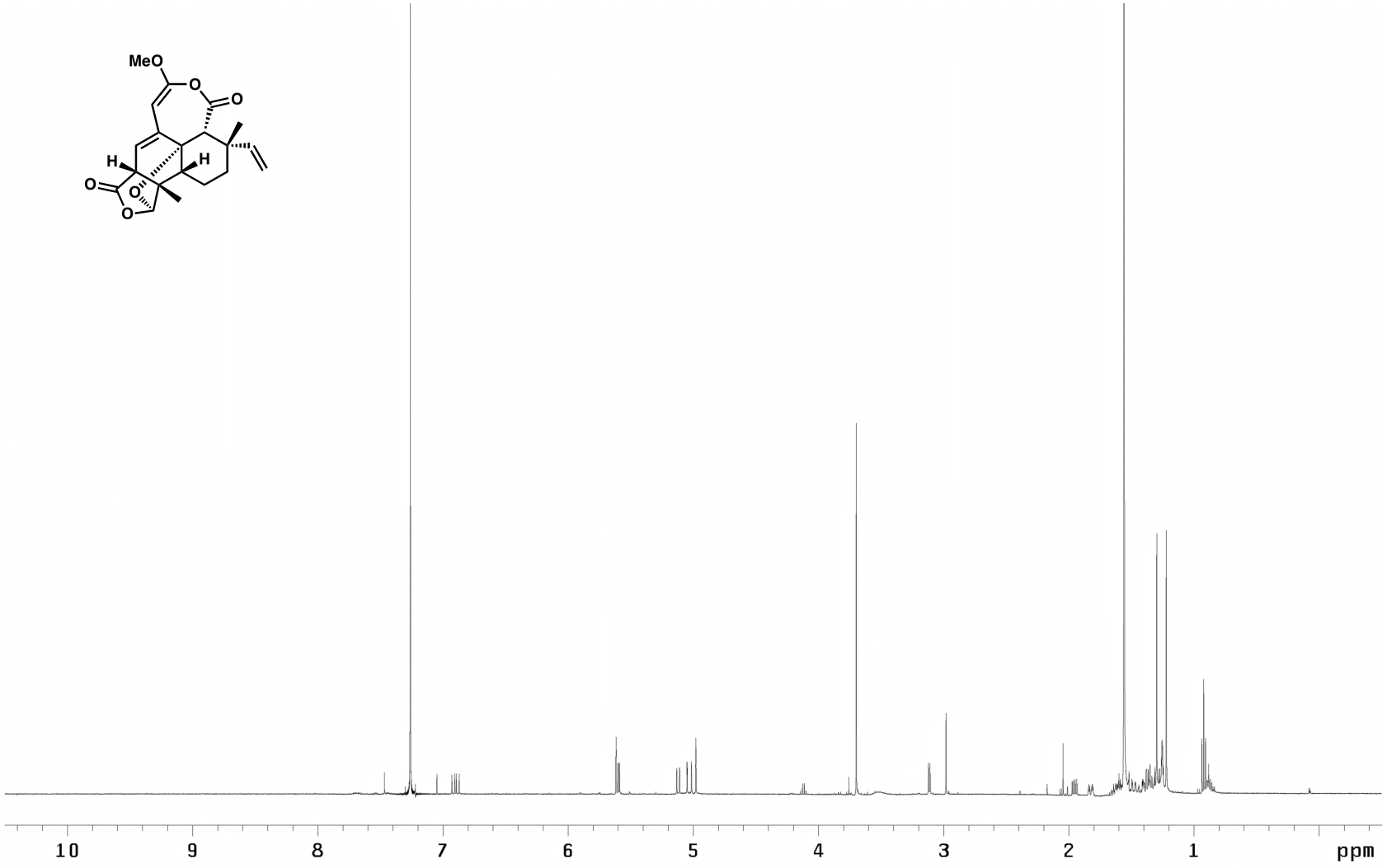


Figure SI-20A ^{1}H NMR (500 MHz, $CDCl_3$) of transtaganolide A (**1**)

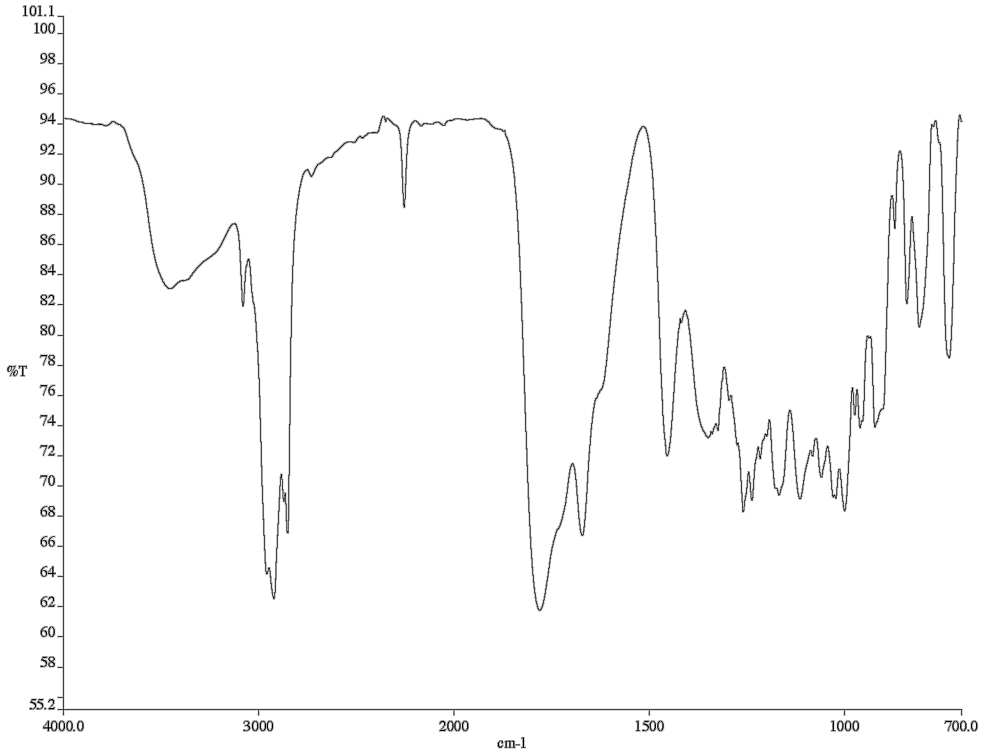


Figure SI-20B Infrared spectrum (thin film/NaCl) of transtaganolide A (**1**)

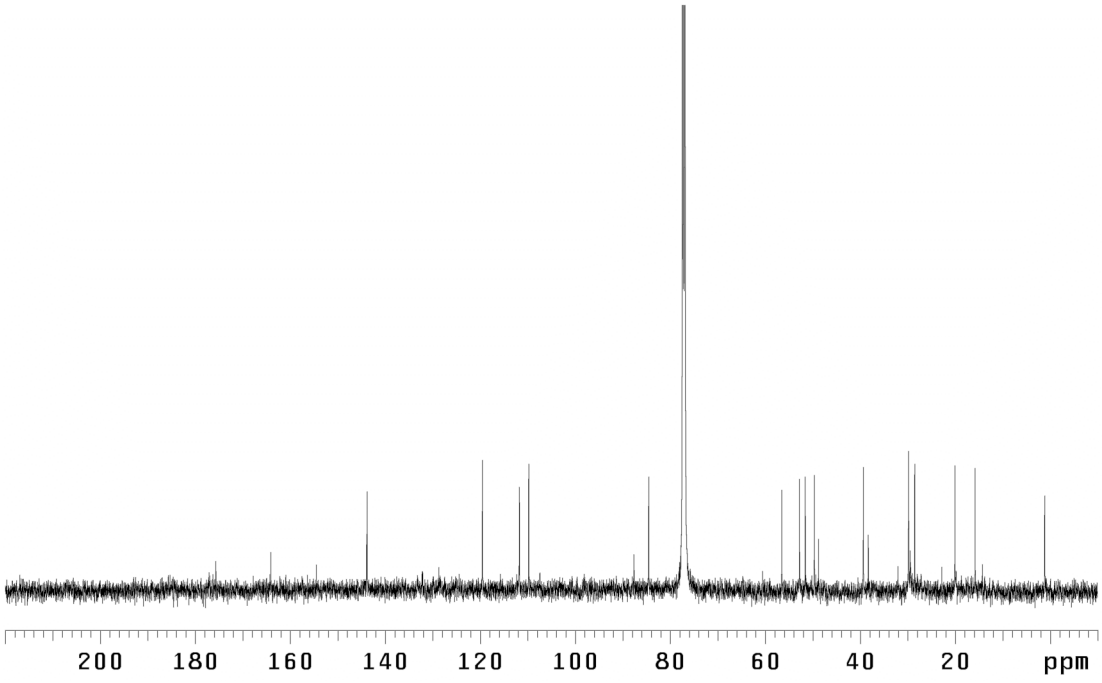


Figure SI-20C ^{13}C NMR (125 MHz, $CDCl_3$) of transtaganolide A (**1**)

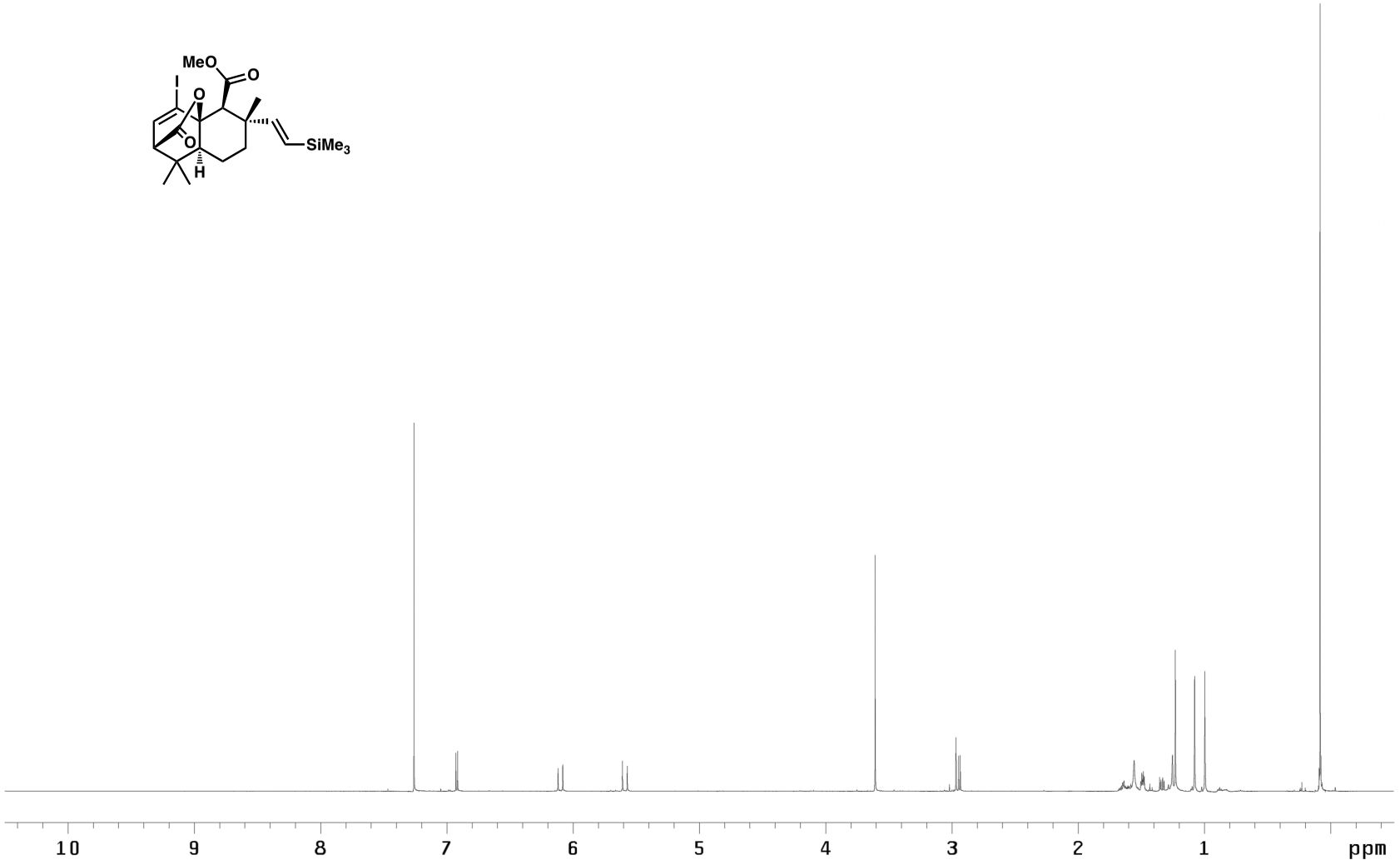


Figure SI-21A ^{1}H NMR (500 MHz, $CDCl_3$) of compound **33**

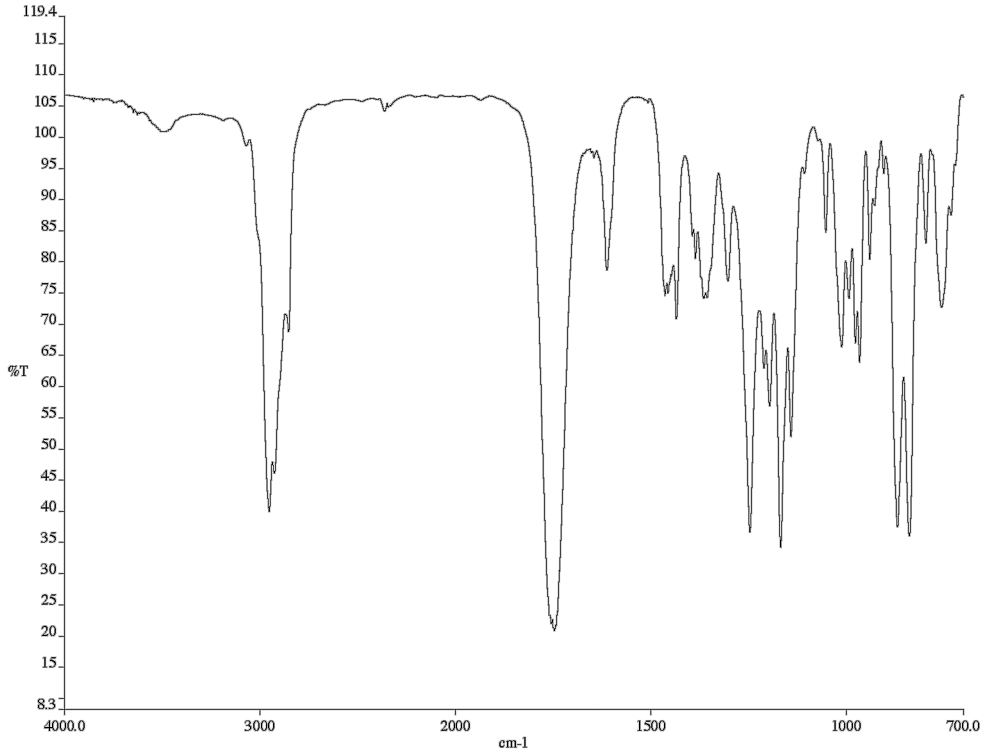


Figure SI-21B Infrared spectrum (thin film/NaCl) of compounds **33**

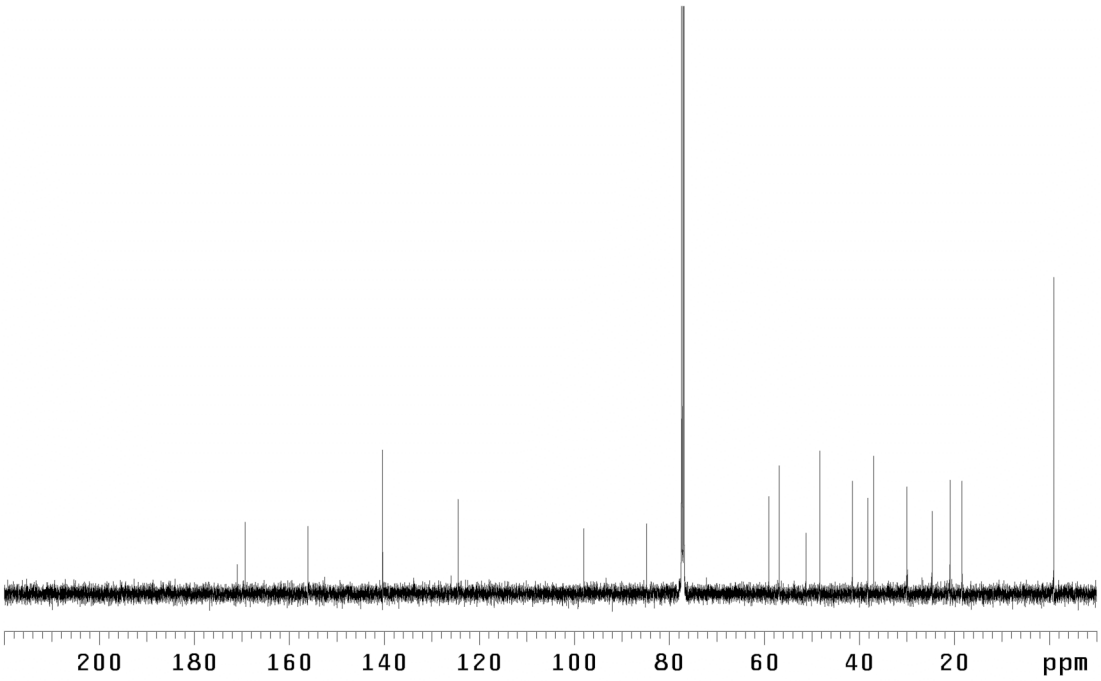


Figure SI-21C ^{13}C NMR (125 MHz, $CDCl_3$) of compounds **33**

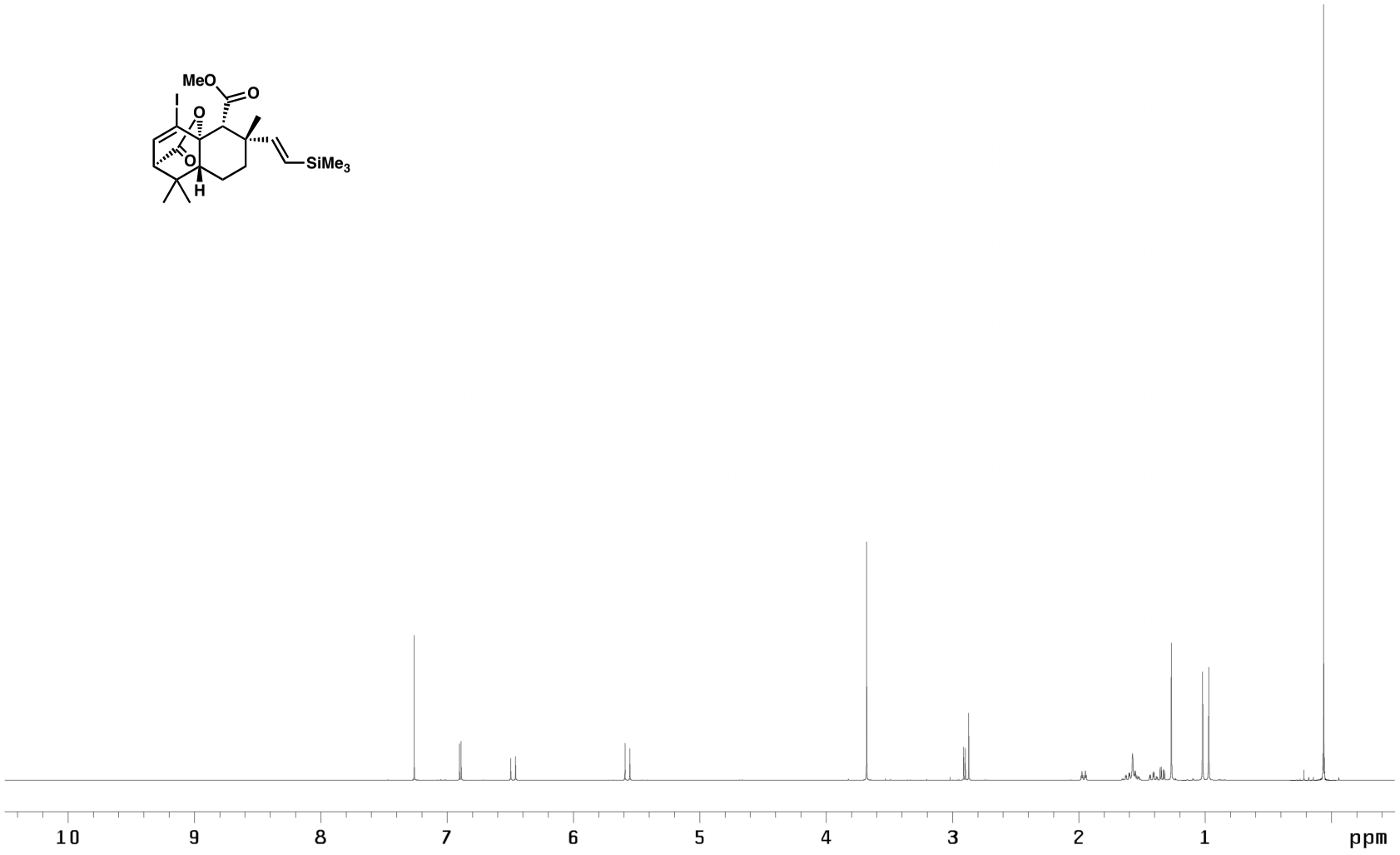


Figure SI-22A ^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-33**

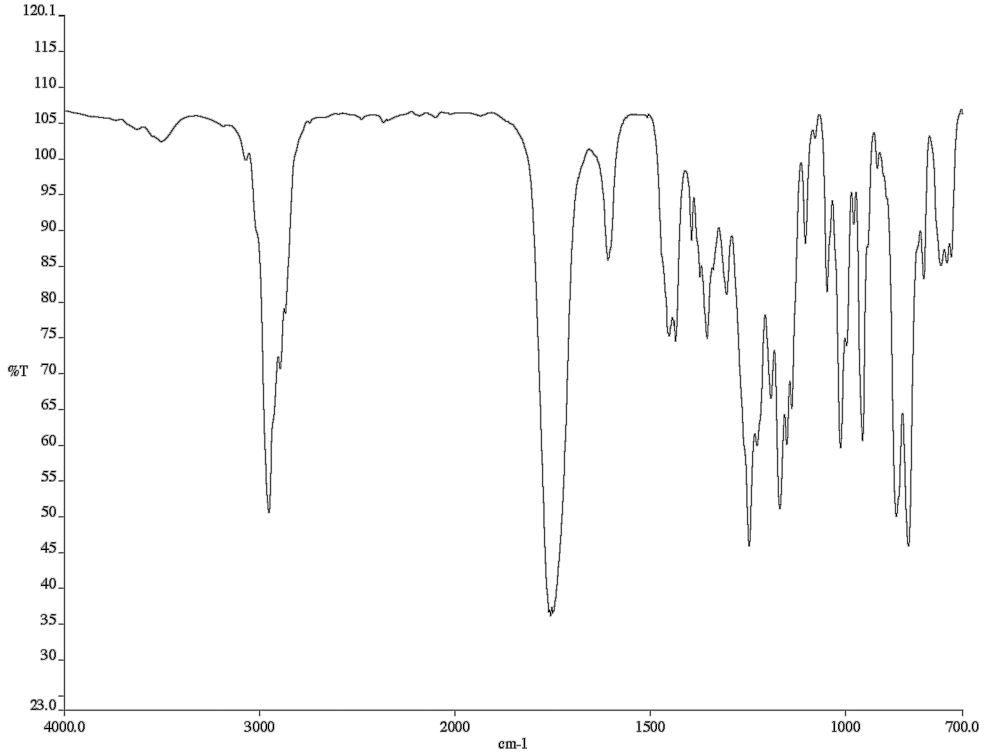


Figure SI-22B Infrared spectrum (thin film/NaCl) of compound **SI-33**

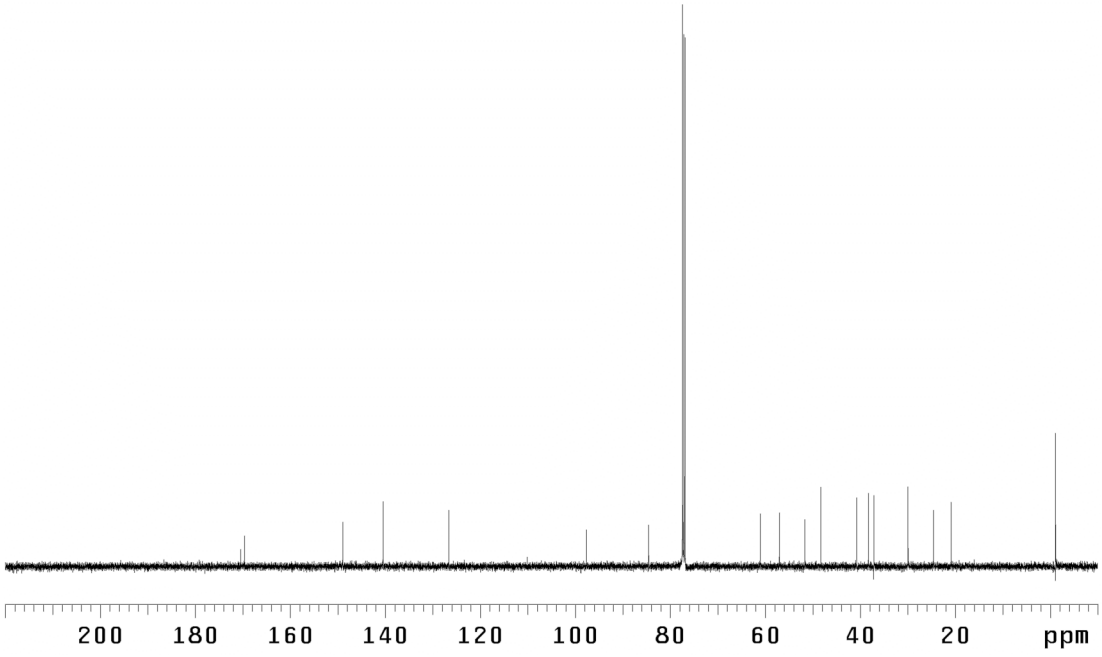


Figure SI-22C ^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-33**